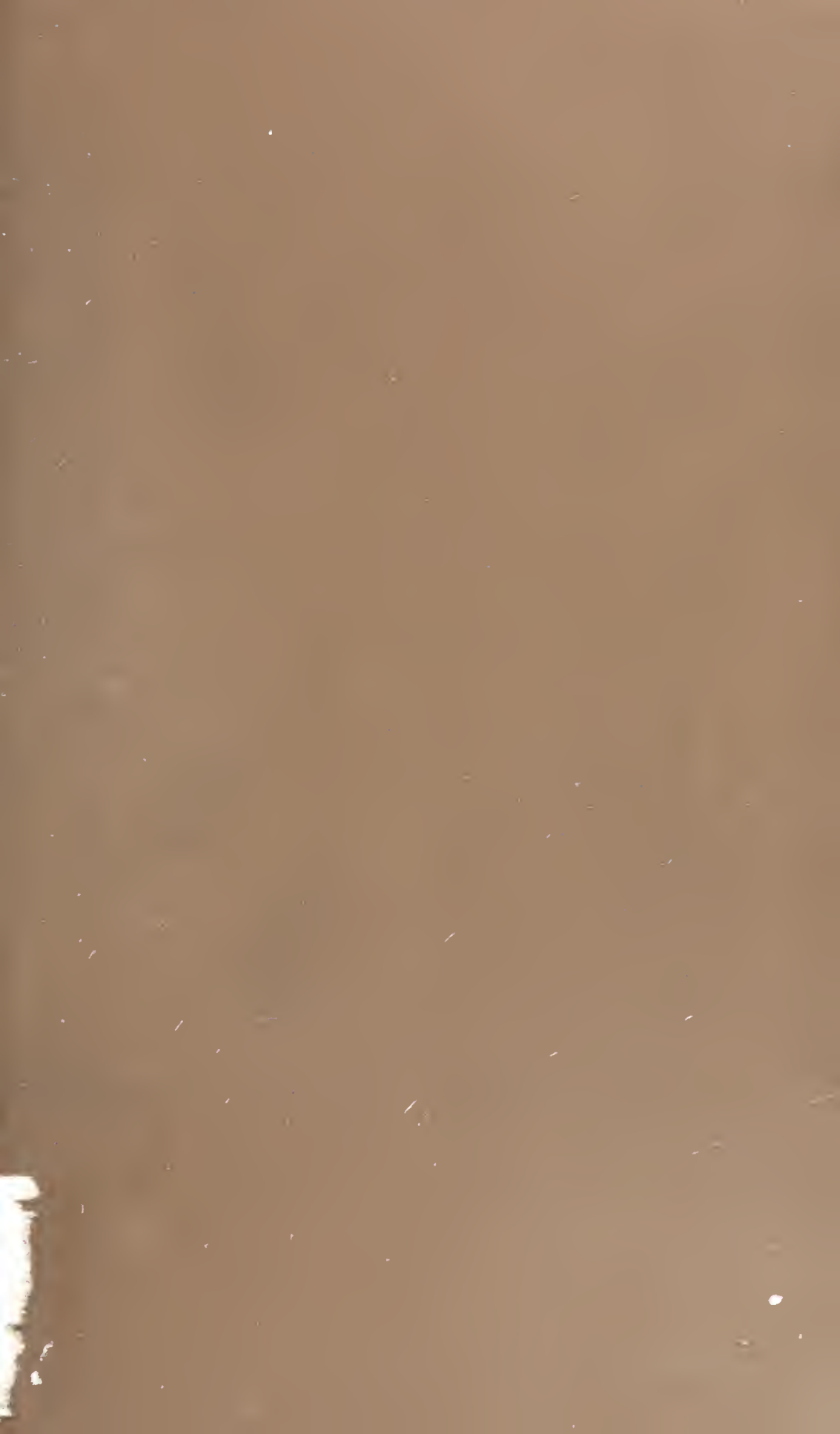




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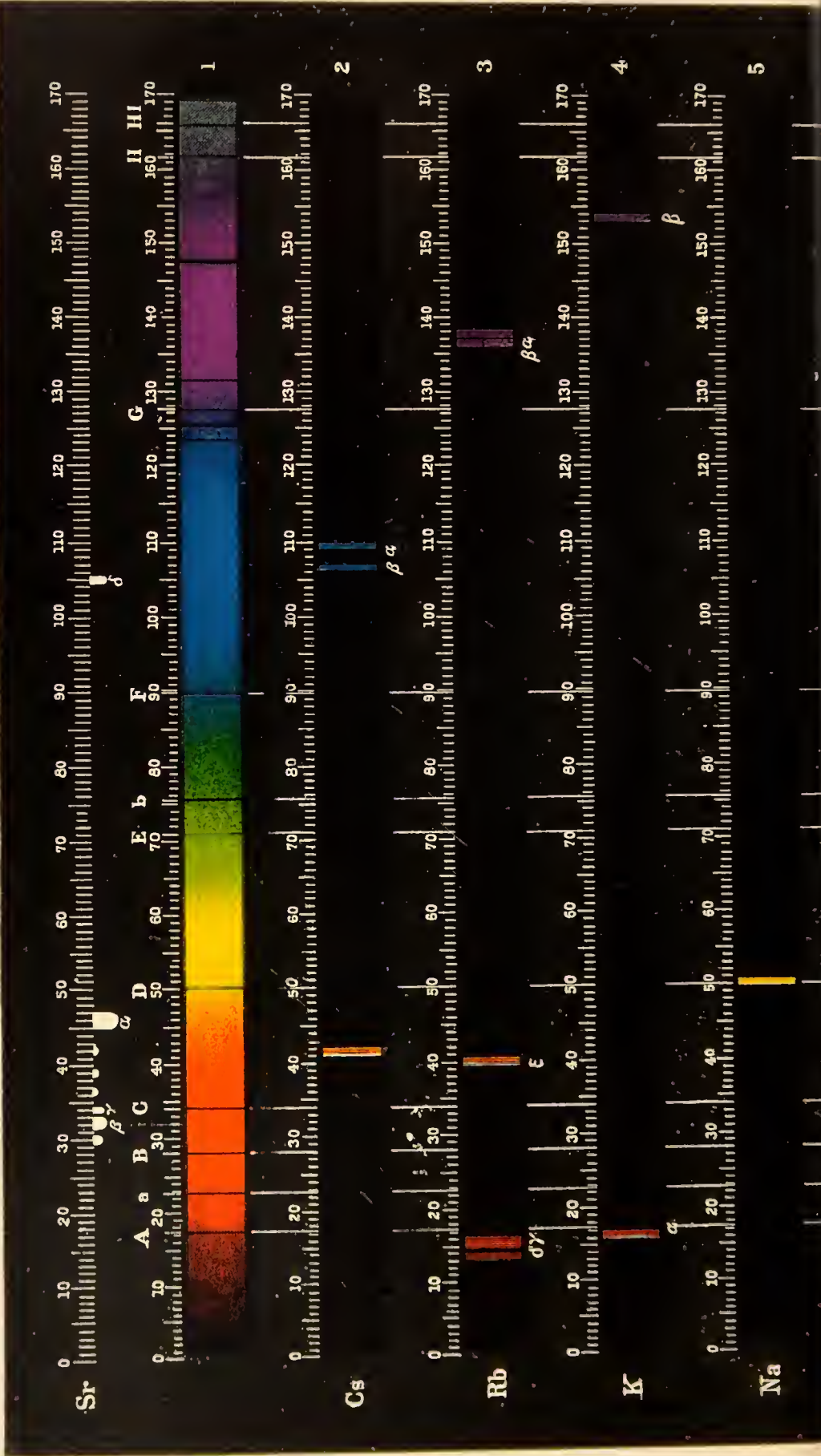
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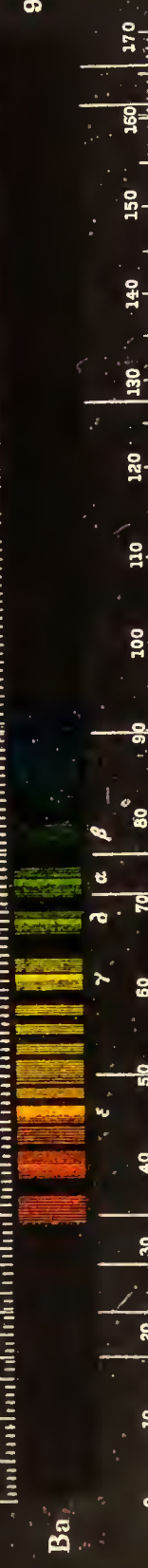
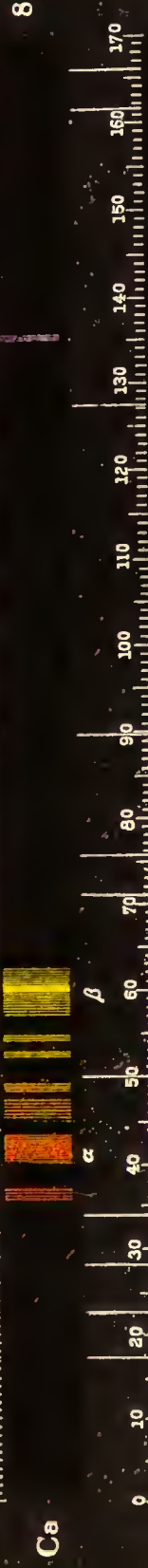
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PLATE II





Li

Sr

Ca

Ba

Tl

In

K $\alpha$

Li $\alpha$

Na

Tl

Sr $\delta$

Rb

K $\beta$

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## PREFACE.

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WHEN the original Dutch edition of this book appeared in 1898, no text-book of inorganic chemistry existed in which the modern views, introduced in this science by VAN'T HOFF, OSTWALD, ARRHENIUS, and others, were sufficiently regarded. As I wanted such a book as a guide for my lectures, I undertook to write one. It was my aim to use these modern theories as a basis, applying them constantly for the explanation of the facts communicated, and so illustrating these theories at the same time by many examples. In order to accomplish this in the most practical way, I judged it best to insert in suitable places short theoretical chapters to which reference could thereafter be made.

In 1900 a German edition of this book appeared; and now the book is rendered into English by the painstaking work of Dr. COOPER. This translation is based on the original Dutch edition as well as on Dr. MANCHOT'S German version of it; however, the book, as it stands, is completely revised and supplied with many additions by the author. I am indebted to Dr. COOPER also for a number of improvements especially adapting the book to the use of American and English students.

A. F. HOLLEMAN.

GRONINGEN (NETHERLANDS),  
January, 1902.

## NOTE.

---

REFERENCES in the text to "Organic Chemistry" refer to Holleman's Organic Chemistry, which is soon to appear in English as a companion to this book.

It is perhaps worthy of note that the entire proof has been carefully read by the author.

The Translator is under obligations to Prof. A. A. NOYES of the Massachusetts Institute of Technology, Prof. H. N. MCCOY of Chicago University, Mr. C. M. HALL of the Pittsburgh Reduction Company, and Dr. F. A. SAUNDERS of Syracuse University for the kindly criticism of special passages, and particularly to his colleague Prof. H. M. SMITH for constant and valuable advice throughout the preparation of the work.

H. C. COOPER.

SYRACUSE, N. Y., March, 1902.

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# INORGANIC CHEMISTRY.

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## INTRODUCTION.

1. **Chemistry** is a branch of the natural sciences,—the sciences which deal with the things on the earth and in the outside universe. The knowledge of these things is obtained by observation with our senses, this being the only means we possess. It is well to understand, therefore, that we know not the things themselves, but simply the impression which they make upon our sense-organs. When we see an object, we perceive, in reality, only the effect on our retina; if we feel the object, it is not the body itself but the excitement of the sensory nerves of touch in our fingers that we are made aware of. Hence it may be fairly asked whether the objects of which we are cognizant are really just as we perceive them, or whether they even exist at all outside of our person. The natural sciences leave this problem out of consideration—its solution is the task of speculative philosophy. In reality they are not concerned with the objects, which in themselves we cannot know, but with the study of the sensations that we receive. The sensations take the place of the objects, and we regard them as such.

2. **The Scientific Investigation of Things.**—What is to be understood by the term? In the first place, a most accurate *description* of the objects. As a result it is found that many resemble each other to a greater or less degree, and it is therefore possible to make a classification, i.e. an arrangement of like objects into groups and a separation of the various groups from each other. By the descriptive method we are finally able to divide the natural sciences into *Zoology*, *Botany*, *Mineralogy* and *Astronomy*.

3. In the second place, scientific investigation includes the

study of the relations which the objects bear to each other; in other words, the study of *phenomena*. The heavenly bodies move towards each other; water turns to ice on cooling; wood burns when heated. It is the task of the natural sciences to accurately observe and describe such phenomena, i.e. to ascertain in what way the heavenly bodies change their relative positions, what conditions affect the freezing of water, what becomes of the burning wood, under what conditions it can burn, etc.

The description of the phenomena leads to a different division of the natural sciences than the description of objects, viz., a division into *Physics*, *Chemistry* and *Biology*, the latter being the study of vital processes, and including *Physiology*, *Pathology* and *Therapeutics*.

4. The human mind, in pursuing the scientific study of nature, does not feel contented with the accurate description of objects and phenomena; it seeks also for an *explanation* of the latter. The various attempts at explanations constitute the most important part of science. When, for instance, we see that a ray of light in passing through a piece of Iceland spar is split up into two other rays of different properties, we strive to account for the phenomenon. When copper is heated in the air, it turns into a black powder; the question again arises, why this thing is so. In searching for an explanation of the phenomena we thus endeavor to penetrate deeper into the essence of things than is possible by direct observation. Although the phenomena themselves are found to be unchangeable, our explanation of them may be modified as our knowledge increases. The transformation of copper into a black powder on heating in the air was formerly explained by the supposition that something left the metal; subsequently, when the phenomena was better understood, by assuming that the copper takes up something from the air.

Scientific investigation pursues in general, then, the following course: A phenomenon is observed and studied as carefully as possible. Thereupon we seek to give an explanation for it. A **hypothesis** is set up. From this we can form conclusions, some of which can be tested by experiment. If the latter really leads to the expected result, the hypothesis gains in probability. If it is subsequently found to explain and link together a whole series of phenomena, it becomes a **theory**.

The nineteenth century was an era of great prosperity for scientific inquiry. For numerous phenomena explanations have been found which possess a great degree of probability. Still it cannot be denied that the present theories penetrate only a little into the real essence of things, and the investigator very soon stumbles upon questions whose explanation does not at present even seem to be a possibility. The chemical process that goes on when copper—to retain our former example—is heated in the air is well known. However, the deeper question, why the action takes place just so and not otherwise, or why the resulting powder is black, still awaits a satisfactory answer.

5. We observed in the preceding paragraph that the natural phenomena are found to be unchangeable. The movement of the planets, for example, still takes place in the same manner as in the times of the Ptolemies; whenever water turns to ice the same increase of volume is to be observed; the crystal form of common salt, whenever and wherever examined, is invariably the same; from the burning of wood the same products are always obtained; the microscopic structure of the leaves of one and the same plant is never found to vary. This general principle finds its expression in the phrase, *constancy of natural phenomena*. Every one is convinced of its truth, and it is tacitly accepted as the basis of every natural scientific investigation. If, for example, one has measured the angles which the faces of a soda crystal form with each other, he considers it certain that all soda crystals must show the same angles, at whatever time or place they may be measured. If it has once been determined that pure alcohol boils at  $78^{\circ}$ , it is forthwith assumed that this must be the case with all alcohol, no matter how it may be obtained or when and where it may be tested.

### PHYSICAL AND CHEMICAL PROCESSES.

6. It was stated above (§ 3) that the description of phenomena leads to a division of the natural sciences into Physics, Chemistry and the study of vital processes (Biology). In defining the province of Chemistry Biology may be left out of consideration; however it is desirable to compare the field of Chemistry with that of Physics. In general it may be said that Physics deals with the temporary, Chemistry with the lasting, changes of matter. By *matter* or *sub-*

*stance* we understand the objects without reference to their form. Iron, marble, sand and glass are substances, independent of their external shape.

A couple of illustrations may make this conception of temporary and lasting changes clear :

(a) A platinum wire glows when held in a colorless gas-flame. On removal it cools off and no change is visible. This is a physical process; the change, the glowing, is of a temporary sort. So soon as its cause was removed, the wire resumed its original condition. When some magnesium wire is held in the flame, it burns with the emission of a brilliant light and turns into a white powder, which is wholly different from the substance magnesium. Here a lasting change has occurred; we have to do with a chemical process.

(b) Again, we may take two white crystallized substances, naphthalene and cane sugar, and heat each separately in a retort with receiver. The naphthalene at first melts; on continued heating it begins to boil, then distills over and condenses in the receiver. The distilled naphthalene resembles the undistilled in every respect. The substance has, as a result of heating, undergone physical changes—melting, change to vapor and finally return to the solid state. The cane sugar behaves differently. Here also a melting is observed at first, but soon the sugar turns darker; a brownish liquid distills over; a peculiar odor is noticeable and at last there remains in the retort a charred, porous mass. The cane sugar suffers a lasting change on being heated. In this case we have a chemical process.

(c) As a third and last example we may consider the conduct of a metallic wire on the one hand and that of acidulated water on the other, when an electric current passes through both. The wire possesses other properties so long as the current is on. If the latter ceases, the wire returns to its original condition. This is a physical process. In the acidulated water, however, the current induces an evolution of gas, and this gas arising from the water has entirely different properties than the water. A lasting change in the substance has occurred; a chemical process has taken place.

A *sharp* distinction between physical and chemical processes is quite often—as will be seen later—very difficult to make.

## CHEMICAL OPERATIONS.

7. In order to avoid repetitions it seems advisable at this point to describe briefly some of the commonest chemical operations.

**Solution.**—When sugar, salt or saltpetre, for example, is put into water, the solid substance is seen to disappear and its taste is found to be taken on by the water. The substance has *dissolved* in the water. There is a definite limit to solubility, for, if the temperature is kept constant and more of the substance is gradually added, a point is finally reached when the water will take up no more. The solution is then *saturated*. The solubility of most solids increases with the temperature. Moreover it is very different with different substances, varying all the way from solubility in all proportions to imperceptible solubility. Thus cane sugar is dissolved in large quantity by water, while sand is practically insoluble in it. Liquids can be either miscible in all proportions (water and alcohol) or only partially soluble in each other. When, for instance, water is shaken with a sufficient quantity of ether and allowed to stand, two liquid layers are formed; the water has dissolved some ether and the ether some water. In most cases the solubility of liquids in each other also increases with the temperature. In the case of gases solubility decreases with rising temperature.

A difference in the solubility of two substances can often be made use of in separating them. Suppose, for instance, it is desired to isolate both ingredients from a mixture of salt and sand; we can add some water, which will dissolve only the salt. The next thing is to separate this solution from the sand. The process by which this is accomplished is called **filtration**.

A circular piece of unsized paper is so folded as to fit into a funnel. This paper cup, called the filter, holds back the solid matter, sand in this case, and lets the solution pass through.

**Decantation** is another but less perfect method of accomplishing this separation. In decanting, i.e. pouring off, a little of the solid is very likely to be carried along by the liquid. It is evident that neither method serves for a complete separation. The latter is accomplished by

**Washing.**—The sand is washed by pouring pure water upon it till the filtered liquid (*filtrate*) contains no more salt. It now only remains necessary to regain the salt in the solid condition.

**Crystallization.**—The filtrate is then warmed to concentrate it by *evaporation* of the water. After the solution has become saturated, if the evaporation is continued, the salt begins to separate out in crystals. Many substances, e.g. saltpetre, are much more soluble in hot than in cold water. Therefore a solution that is saturated when warm must deposit saltpetre on cooling.

**Distillation** (Fig. 1).—This operation is frequently made use of when one is working with liquids. The liquid is placed in a flask or a retort and heated to boiling. The escaping vapor is cooled to

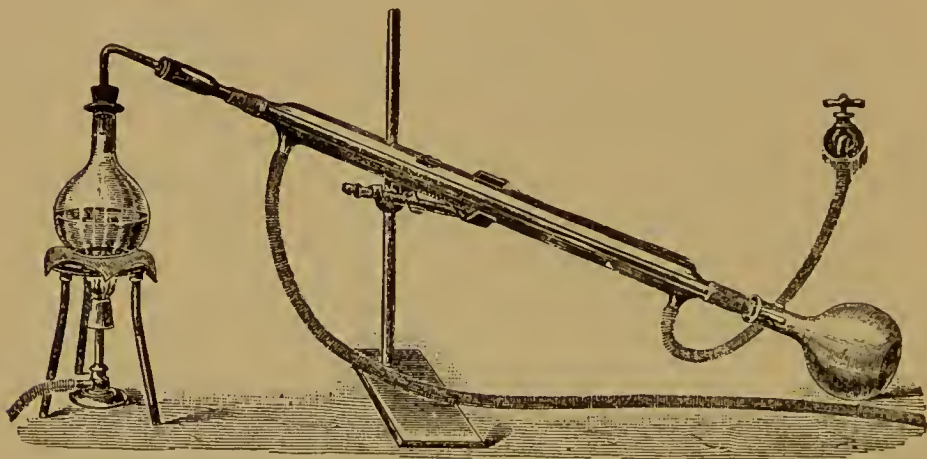


FIG 1.—DISTILLATION.

a liquid in a *condenser*. The latter consists of a sufficiently wide tube encased in a jacket, through which water flows to keep the inner tube cold. The condensed liquid is collected in the *receiver*.

It is readily seen how volatile substances can be separated from non-volatile ones by distillation, e.g. water from salt, since the former distill over and the latter remain in the distilling flask. However, liquids of different volatility can also be separated in this manner. Take, for example, a mixture of alcohol and water. The more volatile constituent, alcohol, passes over for the most part in the early stage of the operation; towards the end the less volatile, water. If the two distillates are collected separately an approximate separation results. A few repetitions of this so-called *fractional* distillation bring about a practically complete separation in many cases.

**Sublimation.**—Certain solids, e.g. camphor, when heated (at



ordinary pressure), turn to vapor without melting. If this vapor comes in contact with a cold surface, the substance is deposited in the solid, crystallized state. It is evident that we have here another method of separating some substances.

### THE ELEMENTS.

8. When a substance (§ 6) is subjected to various influences, such as heat, electricity, or light, or is brought in contact with other substances, it is very often split up into two or more dissimilar components. As an example let us take gunpowder. Water is added and the whole is stirred well and gently warmed; after a while it is filtered, and that which remains on the filter is found to be no longer gunpowder, for it can no longer explode. On evaporating the filtrate a white crystalline substance, saltpetre, remains. The undissolved part is dried and then shaken with another solvent, carbon bisulphide. After a time the mixture is filtered, as before, and there is left on the filter a black mass, consisting of charcoal powder. The carbon bisulphide of the filtrate evaporates and leaves yellow crystals of sulphur. Thus we see that, by successive treatment with water and carbon bisulphide, gunpowder can be separated into three substances, viz., carbon, sulphur and saltpetre. The two former are incapable, even when subjected to all the agencies at our command, of division into different components. Not so with saltpetre, for when the latter is heated strongly a gas is given off in which a glowing wooden splinter is at once ignited. When the evolution of gas ceases, a substance remains which gives off red fumes on treatment with sulphuric acid, something that saltpetre does not do. Saltpetre can evidently be broken up still farther by heating.

If we subject all sorts of substances to a successive treatment with reagents of the most different kinds, we finally discover certain ones that cannot be resolved into simpler substances by our present means. Such substances are called *elements*. Although the number of substances, according to § 6, may be considered as infinitely great, experience has taught that the number of elements is small. There are about *seventy*.

As our methods of examination improve, it may quite possibly be found that the substances which the chemist of to-day regards as elements have no right to the name. Therefore, when we use the

word "element," it is to be regarded as a relative term, dependent on the extent of our knowledge and the means at our command. In the history of chemistry some cases are to be found where substances, once believed to be elements, were subsequently decomposed.

The exact number of elements cannot be definitely stated, because, on the one hand, not all the substances that possibly exist may be within our reach,<sup>1</sup> and, on the other hand, it is doubtful whether certain substances now regarded as elements cannot be divided by means already known.

The following is an alphabetical list of the elements at present known to exist :

Aluminium	Fluorine	Neon	Sodium
Antimony	Gallium	Nickel	Strontium
Argon	Germanium	Niobium	Sulphur
Arsenic	Gold	Nitrogen	Tantalum
Barium	Helium	Osmium	Tellurium
Beryllium	Hydrogen	Oxygen	Thallium
Bismuth	Indium	Palladium	Thorium
Boron	Iodine	Phosphorus	Tin
Bromine	Iridium	Platinum	Titanium
Cadmium	Iron	Potassium	Tungsten
Caesium	Krypton	Praseodymium	Uranium
Calcium	Lanthanum	Rhodium	Vanadium
Carbon	Lead	Rubidium	Xenon
Cerium	Lithium	Ruthenium	Ytterbium
Chlorine	Magnesium	Samarium	Yttrium
Chromium	Manganese	Scandium	Zinc
Cobalt	Mercury	Selenium	Zirconium
Copper	Molybdenum	Silicon	
Erbium	Neodymium	Silver	

As may be seen from this list, the *metals* are included in the elements. Together with them we find a number of other substances, as oxygen, sulphur, phosphorus, etc., that are classed under the term *non-metals*, or *metalloids*. To the latter class belong many very important substances, e.g. oxygen, an element that combines with almost all others, causing what is called combustion. Oxygen is present in a large amount in the air. Another non-

---

<sup>1</sup> Of the interior of the earth only a very small part is known. If we think of the earth as about the size of an orange, the deepest mine-shafts would not even penetrate the thin yellow exterior layer of the orange-skin.

metal is carbon, which is present in all organized substances, and is therefore a constituent of every animal and plant. Sulphur, which burns with a blue flame, giving off a pungent odor, and chlorine, a greenish yellow gas of very disagreeable odor, which combines readily with most metals, are also non-metals.

The elements occur in very unequal proportions in the part of the earth accessible to us. Oxygen, which occurs in air, in water, and in the solid part of the earth's crust, is very preponderant, composing more than 50% of those portions of the earth which have been investigated. The elements silicon, aluminium, iron, calcium, carbon, magnesium, sodium, potassium and hydrogen, together with oxygen, make up 99% of the earth's crust. There remains, therefore, only 1% for all the other elements. Some of these are quite common, e.g. lithium, but they almost always occur in very small quantities. Others, like niobium and tantalum, are found in relatively very small amounts and in isolated places.

The following table, according to CLARKE, gives an approximate summary of the quantities of the elements found in the part of the earth accessible to us :

	Earth's Crust.	Ocean.	Atmosphere.	Entire Earth.
	%	%	%	%
O .....	47.29	85.79	23.00	49.98
Si .....	27.21	....	....	25.30
Al .....	7.81	....	....	7.26
Fe .....	5.46	....	....	5.08
Ca .....	3.77	0.05	....	3.51
Mg.....	2.68	0.14	....	2.50
Na.....	2.36	1.14	....	2.28
K .....	2.40	0.04	....	2.23
H... ..	0.21	10.67	....	0.94
Ti .....	0.33	....	...	0.30
C.....	0.22	0.002	....	0.21
Cl. ....	0.01	2.07	....	0.15
Br .. ...	...	0.008	....	0.15
P .....	0.10	....	....	0.09
Mn.....	0.08	....	....	0.07
S.....	0.03	0.09	....	0.04
Ba.....	0.03	....	....	0.03
N .....	....	....	77.00	0.02
Cr .....	0.01	....	....	0.01
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

With the aid of spectral analysis (§§ 263-267) it has been ascertained that the heavenly bodies contain most of the same elements as our earth, and also some others.

## OXYGEN.

9. Under ordinary conditions of temperature and pressure, oxygen is a colorless and odorless gas, whose most noticeable property is its ability to set glowing substances on fire with evolution of much light and heat. A glowing splinter of wood, for example, when introduced into an atmosphere of oxygen, begins at once to burn brightly. This action is ordinarily used as a *characteristic test* for the identification of oxygen.

This gas can be obtained in various ways. There are many substances which are known to evolve oxygen on heating.

(1) *Mercuric oxide*, when heated strongly in a retort (Fig. 2), yields oxygen, which can be collected by means of a delivery-tube

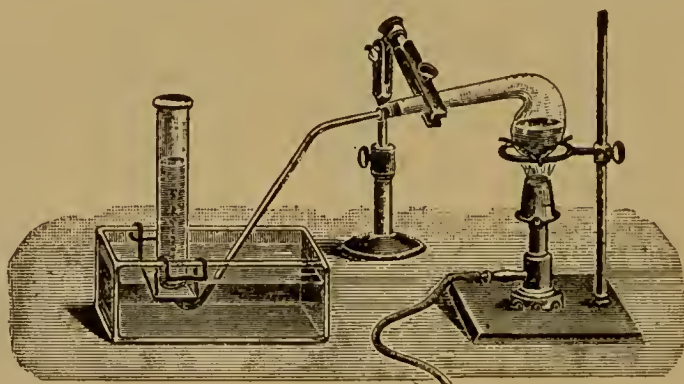


FIG. 2.—PREPARATION OF OXYGEN FROM POTASSIUM CHLORATE.

opening under the mouth of a cylindrical receiver filled with water. The inside of the retort becomes covered with drops of mercury.

(2) The same apparatus can be used in making oxygen from *potassium chlorate* (chlorate of potash), as well as from *potassium nitrate* (saltpetre), *potassium permanganate*, and many other substances. The preparation of oxygen by heating potassium chlorate is a method frequently used in the laboratory.

Some substances give off oxygen when heated together with others, e.g.:

(3) Potassium bichromate or manganese dioxide, when heated with sulphuric acid.

(4) Zinc oxide, when heated in a current of chlorine.

The atmospheric air consists principally of oxygen and nitrogen. The following method for separating these gases was employed by LAVOISIER in 1774. He introduced some mercury into a retort A (Fig. 3) with a long, doubly-bent neck that opened under a bell-

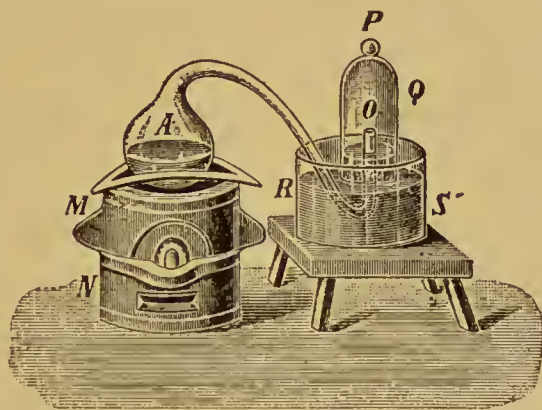


FIG. 3.—ABSORPTION OF OXYGEN BY MERCURY.

jar PQ filled with air and resting in a dish RS of mercury. He then heated the retort steadily for several days, keeping the mercury almost boiling. As a result, a part of the air in PQ disappeared, and the gas remaining was found to possess other properties than air—it was nitrogen. At the same time the mercury had been partially transformed into a red powder, mercuric oxide. On heating the latter more strongly oxygen was obtained.

The *physical properties* of oxygen, besides those already mentioned, are as follows: Its specific gravity, assuming the density of air to be 1, is 1.10535; taking hydrogen as a unit, it is 15.88. A liter of oxygen at 0° and 760 mm. Hg. pressure weighs 1.4296 g. Oxygen can be liquefied—its critical temperature being  $-118^{\circ}$  and its critical pressure 50 atmospheres. Liquid oxygen has a specific gravity of 1.124 (based on water) and a boiling-point of  $-182.95^{\circ}$  at 745.0 mm. pressure. Its color is light blue. Liquid oxygen has been obtained in quantities as large as several liters. It can even be preserved for some time at ordinary pressure, with the aid of a so-

called vacuum-flask (Fig. 4). The latter is a vessel enclosed in an air-tight jacket, the space between the walls being evacuated. 100 l. water at  $0^{\circ}$  dissolves 4.89 l. oxygen. The gas is also somewhat soluble in alcohol and in molten silver. When the silver solidifies, the oxygen—a volume about ten times that of the metal—suddenly escapes from solution, causing peculiar elevations on the surface of the silver (“spitting” of silver).



FIG. 4.—VACUUM-FLASK.

We remarked above (§ 7) that the solubility of gases in liquids diminishes with increasing temperature. A very remarkable law expresses the relation that exists between the solubility of a gas and its pressure, namely, *the solubility is proportional to the pressure*. This is the law of HENRY. Thus, when the pressure becomes  $a$ -fold, the solubility also becomes  $a$ -fold. As the quantity of a gas which is present in a certain volume is likewise proportional to the pressure, the law of HENRY can also be expressed thus: *the volume of a gas, dissolving in a certain quantity of a liquid, is independent of the pressure*.

This law is rigid when the solubility of the gas is small; when the solubility is large, for instance 100 volumes in 1 of the liquid, its deviations are considerable.

10. Among the *chemical properties* of oxygen the most prominent is its vigorous support of combustion. The following are interesting examples:

Charcoal glows in air only moderately and without much evolution of light. In oxygen, however, it burns with a bright glow. Sulphur, which burns in air with only a small flame, burns in oxygen with an intense blue light. Phosphorus burns in oxygen with a blinding white light. A steel watch-spring that has been heated to redness at one end and put into oxygen, burns with scintillation. Zinc also burns in it with a dazzling light. In all these and analogous cases the oxygen, as well as the burning material, disappears during the combustion, while new substances are formed. A lasting change therefore takes place and we have to do with a chemical process. The product of burning charcoal is found to be a gas that makes lime-water cloudy and is unable to support combustion: it is called carbonic acid gas. Sulphur also yields a gas; it has a

piercing odor and is called sulphur dioxide. Phosphorus produces a white flocculent powder, phosphorus pentoxide. When iron burns, a black cindery powder is formed, called "hammer-scale," because it composes the sparks that fly from the anvil.

The question now arises as to what really occurs in the above cases. In the first place, it has been found that the weight of the product of combustion is greater than that of the substance burned.

The increase in weight of the substance during burning can in many cases be easily demonstrated. For instance, a horseshoe magnet that has been dipped in iron-filings may be hung on the lower side of a scale-pan and balanced by weights put in the other pan. The iron-filings may be burned by passing a non-luminous flame under them a few times. On cooling, the scale-pan attached to the magnet sinks. In a similar way one may demonstrate the increase of weight in the burning of copper. In order to prove the increase of weight in a case where only gaseous products are formed, a candle may be burned and the combustion products, carbon dioxide and water-vapor, collected by letting them pass over unslaked lime, with which both unite.

Closer investigation has revealed the fact that the increase in weight is due to the presence of oxygen, as well as the burned substance, in all combustion products. The latter are *compounds* of these substances with oxygen. The participation of oxygen in the burning of zinc, for example, may be proven by heating the combustion product, zinc white, in a tube and leading over it chlorine gas, whereby oxygen is driven off. The compounds of oxygen are called *oxides*, and the act of this combination is known as *oxidation*.

When substances burn in the air, it is only the oxygen, which combines with them. Nevertheless, the nitrogen of the air is heated and thus takes a part of the heat evolved in the combustion. Therefore the temperature of a burning object cannot rise so high as in pure oxygen, and, as the emission of light depends on a high degree of temperature, combustions in oxygen are for this reason much more bright than in air.

There are two general methods of ascertaining what elements exist in a compound. According to the one method the compound is decomposed and the elements composing it thereupon determined. This is the *analytic* method. According to the other, the *synthetic* method, the composition is found by combining dif-

ferent elements to form new substances. In the above-described experiment (§ 8) of LAVOISIER the composition of the red powder is learned by decomposing it at high temperature, whereupon it separates into only mercury and oxygen. Inversely it was possible to obtain the red powder by heating pure oxygen and pure mercury together at a lower temperature. The former is an example of analysis, the latter of synthesis.

## HYDROGEN.

11. Hydrogen is a colorless and odorless gas that is rarely found in the free state. The gases of some volcanoes contain it and it can also result from processes of decay. In combination with other elements, however, hydrogen is very widely distributed and occurs in very large amount (§ 8).

Hydrogen can be prepared in various ways. In the first place, hydrogen compounds can be broken up.

(1) Water is decomposed by the electric current, hydrogen being evolved at the negative pole (cathode).

(2) Palladium hydride is broken up by heat into palladium and hydrogen (see § 315).

The ordinary methods of preparing hydrogen depend on the indirect decomposition of hydrogen compounds, i.e. their reaction with other substances. The following are examples of this sort:

(3) The action of zinc on dilute sulphuric acid (§ 89). This is the ordinary method (see Fig. 6).

(4) The action of zinc or aluminium filings on caustic potash or slaked lime.

(5) The action of sodium or potassium on water or alcohol.

(6) Magnesium powder, when boiled with water, also evolves hydrogen, especially when some chloride of magnesium is dissolved in the water, because such a solution dissolves the magnesium oxide which forms on the surface of the metal.

12. The *physical properties* of hydrogen are these: It is the lightest of all known substances. Its specific gravity (air = 1) amounts to only 0.06949. One liter hydrogen at 0° and 760 mm. Hg. pressure weighs 0.0899 g. Its lightness renders it useful for inflating balloons. It is very hard to liquefy. In 1898 DEWAR succeeded in obtaining hydrogen as a coherent liquid in quantities of



50 c.c. by cooling the gas, which was under a pressure of 180 atmospheres, to  $-205^{\circ}$  (by the rapid evaporation of liquid air in a vacuum) and then reducing the pressure greatly by allowing the gas to escape through a fine aperture. In the mechanical theory of heat it is shown that the expansion resulting from such a sudden release of pressure involves a considerable absorption of heat and therefore a very great depression of temperature. The critical temperature of hydrogen lies  $30-32^{\circ}$  above the absolute zero ( $-273^{\circ}$ ) and the critical pressure is only 15 atmospheres; however, the last two values are not yet exactly determined. Liquid hydrogen is colorless. It boils at  $-252.8^{\circ}$ . Its specific gravity, with reference to water, is only 0.07, being therefore considerably less than that of all other known liquids. DEWAR further succeeded in reducing hydrogen to the solid state by allowing the liquid to evaporate quickly at 30-40 mm. pressure.

Hydrogen is slightly soluble in water, 100 l. water dissolving 2.15 l. of the gas at  $0^{\circ}$ . Alcohol takes up somewhat more.

13. *Chemical Properties.* Hydrogen does not unite with as large a number of elements as oxygen. At a higher temperature it displays a strong tendency to unite with oxygen, burning with an almost colorless and very hot flame to form water. This property serves for the identification of hydrogen gas.

When a current of hydrogen is directed upon very finely divided platinum (spongy platinum or platinum black, § 316), the hydrogen is ignited. This is due to the condensation (*occlusion*) on the platinum sponge of oxygen, that is able in this condition to unite with hydrogen. The platinum suffers no change. A chemical action of this sort, i.e. one which is apparently brought about by the mere presence of a certain substance, is called a *catalytic* or *contact* action. In the great majority of such cases it has, however, been found that the catalyzing substance (catalyzer) probably has some part in the reaction (here, for example, by the condensation of oxygen), but appears at the end of the process unchanged. The catalyzer may either hasten or retard a reaction.

The high temperature of the hydrogen flame is made use of in fusing platinum, quartz, etc., and in the *Drummond lime-light*.

In the latter oxygen is forced into a hydrogen flame, which is directed on to a piece of quicklime. The intense heat causes the latter to glow brilliantly.

Such a flame is known as an oxyhydrogen flame. An apparatus (*oxyhydrogen blow-pipe*) like that represented in Fig. 5 is required to produce

it. The hydrogen enters at *W* and passes out at *a*, where it is lit. Oxygen is blown into the flame at *S*. Thus the gases do not mix till they reach the flame, and the possibility of an explosion is avoided.

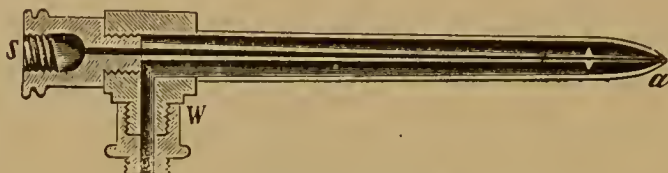


FIG. 5.—OXYHYDROGEN BLOW-PIPE.

A mixture of hydrogen and oxygen, especially in the proportion of 2 vols. H and 1 vol. O (detonating gas), when ignited, turns momentarily to steam; in other words, it explodes. This experiment can, however, be performed harmlessly by using a wide-mouthed cylinder of not too great dimensions. A loud report is heard in this case, because the steam at the moment of its formation occupies a much larger volume at the high temperature of the combustion than the mixture of the original gases, and as a result the air is suddenly ejected with violence. When the explosion occurs in a closed vessel, no sound is heard (*cf. e.g. Fig. 12*).

The temperature to which detonating gas must be heated to explode is found to be about  $700^{\circ}$ . At a lower temperature combination between hydrogen and oxygen also takes place, but not instantaneously, as in explosions; the lower the temperature, the slower the process. When, therefore, no change in cold detonating gas is observed even in the course of several years, we must attribute the fact to the extraordinary slowness of the process at ordinary temperatures. A simple calculation will make this plain. BODENSTEIN observed that, when detonating gas is heated at  $509^{\circ}$  for 50 minutes, 0.15 of the whole is changed to water. Now it is a general rule that, when the temperature sinks  $10^{\circ}$ , a chemical reaction becomes about twice as slow; at  $499^{\circ}$  it would thus take 100 minutes till the 0.15 part of the gas had formed water. At the ordinary temperature, say at  $9^{\circ}$ , it would be  $50 \times 2^{50}$  minutes, that is about  $1.06 \times 10^{11}$  years. The same can be said of all chemical reactions. When we see that wood, sulphur, etc. burn quickly at higher temperatures, we must admit that oxidation takes place also at ordinary temperatures, though so slow that we cannot perceive it.

Hydrogen is not only able to unite with free oxygen, but it also has the power to withdraw oxygen from many of its compounds. The action of hydrogen on a compound is called, in general, **reduction**. This action is often a very useful means of determining whether a compound contains oxygen, since the latter, if present, will usually unite with the hydrogen to form water. Copper oxide may serve as an example of the application of this method. A little is placed in a tube, hydrogen is led over it, and heat is then applied. One soon sees the black oxide change to red copper, and water depositing in drops on the colder parts of the tube. Many other oxides can be similarly reduced, e.g. iron oxide, lead oxide, etc.

### THE CONSERVATION OF MATTER.

14. The quantitative relations of oxidizing and reducing processes, such as were discussed in § 13, i.e. the determination of the masses of the substances participating in the actions, may be used to elucidate a very important law. A definite amount of copper powder, for example, may be placed in a tube and the weight of the tube with the powder ascertained. Oxygen is then led over the copper at a high temperature. The apparatus should be so arranged that the volume of the oxygen which combines with the copper can be measured. When the oxidation process has proceeded for some time, the tube containing the oxidized copper is allowed to cool and then weighed. The weight is found to have increased, and the increase is just equal to the weight of the volume of oxygen used up. Thereupon hydrogen is passed through the tube with the copper oxide and heat applied. Here also arrangements should be made for measuring the volume of hydrogen consumed in reduction. The reduction is allowed to go on until all the copper oxide is transformed back to copper. When the tube and powder are subsequently weighed, they will be found to have reassumed their original weight. The water that forms can be absorbed by a substance like quicklime or concentrated sulphuric acid and weighed. It will be found equal in weight to the loss of weight of the copper oxide on changing to copper plus the weight of the consumed hydrogen.

In these cases therefore the combined weight of the reacting substances before and after the reaction is the same. Copper + consumed oxygen weighs just as much as copper oxide; copper oxide

+ consumed hydrogen weighs just as much as copper + water; and, finally, the regained copper weighs just as much as that originally taken. The substances can be changed into different states, but their weight remains unaltered. This phenomenon is observed without exception in chemical actions, and we therefore accept as a law the statement that matter is indestructible, or that no matter can be lost or gained. This principle was introduced into chemistry by LAVOISIER (1743-1794).

The old Greek philosophers were already firmly convinced of the impossibility of producing or destroying matter. In all ages this belief has been the basis of philosophic thought. To LAVOISIER is due the credit of having demonstrated the practical application of the principle of the indestructibility of matter. He assumed that gravity is an inseparable attribute of all matter—concerning which a great deal of doubt still existed—and that the combined weight of the substances concerned must therefore be the same before and after a chemical reaction.

The theory of knowledge teaches that the principle of the indestructibility of matter lies originally at the basis of our thinking. It is entirely incorrect to suppose that it was established by experimentation; on the contrary, we test the correctness of our experimental results by ascertaining in how far they conform to this principle. This can be easily understood in the above case of the oxidation and reduction of copper. In performing this experiment one finds that the weight of copper + oxygen is *not* exactly equal to that of the copper oxide formed. Even after several repetitions slight differences are still found. Because we feel that there must be absolute equality, we attribute these differences to imperfections in our instruments, and we consider our instruments improved if they enable us to approach nearer the complete equality of the weights before and after the experiment. Nevertheless, we are unable to really observe an absolute equality.

## WATER.

15. Water was regarded as an element for many centuries. Not until 1781 did CAVENDISH discover that, when a mixture of hydrogen and air, or oxygen, explodes, water is formed. Being, however, a supporter of an erroneous theory (§ 106), he failed to realize the importance of his discovery. LAVOISIER in 1783 repeated this experiment and comprehended it as a synthesis of water, as we still do to-day.

With the aid of the apparatus pictured in Fig. 6, this synthesis can be easily demonstrated. The hydrogen is generated in the

two-necked (WOLFF) bottle from zinc and sulphuric acid. In order to free the gas from water vapor, it is passed through the horizontal tube, which contains chloride of calcium, or bits of pumice-stone soaked in sulphuric acid. The dry gas is ignited and, as it burns, water is gradually deposited on the walls of the bell-jar.

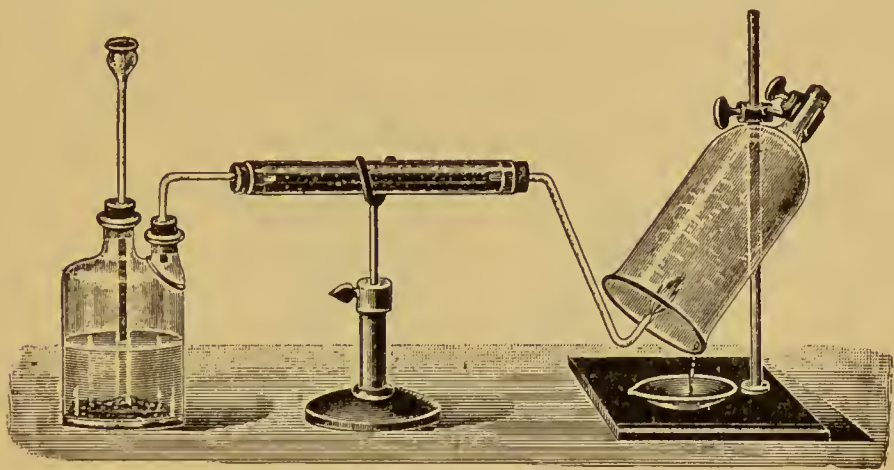


FIG. 6.—COMBUSTION OF HYDROGEN.

In addition to this direct synthesis from its elements there are other ways of obtaining water. For example, many compounds, such as the blue crystals of copper vitriol, give off water when heated.

The formation of water by the action of hydrogen on oxygen compounds was seen above (§ 13) in the reduction of copper oxide. On the other hand, it is also produced by the action of oxygen on certain hydrogen compounds. This is seen, for example, in the burning of alcohol.

Finally, water can result from the reaction of a hydrogen compound with one of oxygen. This is the case when ammonia-gas (§111) is led over hot copper oxide.

The synthetic methods of preparing water, such as the above named and many others, possess, however, merely theoretical importance. Even when water is wanted in a perfectly pure state, natural water is resorted to. This contains solids and gases in solution, which must be eliminated. Its purification is accomplished by distillation. An apparatus well suited to this purpose is shown in Fig. 7.

Water is placed in the retort *A*, which rests over the fireplace, and boiled. The dissolved gases are first driven off; the hot steam follows, passing through the dome *B* into the condensing coil ("worm") *C*, which is cooled by water in the vessel *D*. The condensed water, now pure, flows down into the bottle; the solid substances that were dissolved in the water remain in the retort.

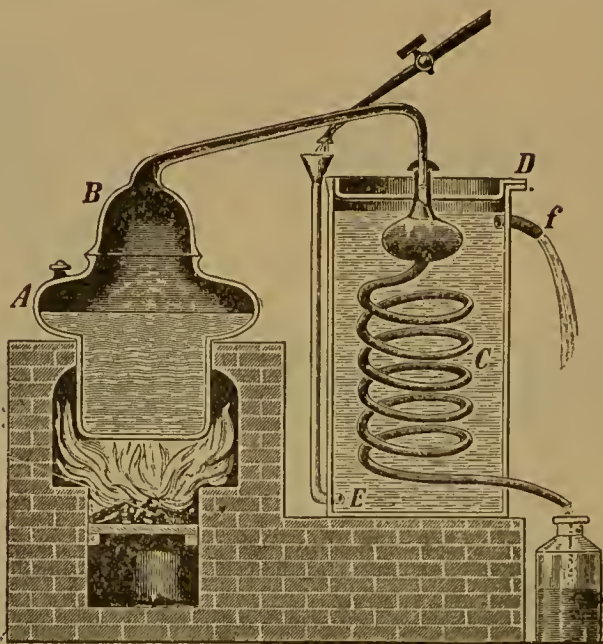


FIG. 1.—PURIFICATION OF WATER BY DISTILLATION.

The cooler *D* is supplied with cold water through a tube, entering near the bottom, while the heated, and therefore specifically lighter, water flows out near the top. The steam thus meets with cooling water of a lower temperature as it passes down the worm, and is in this way very completely condensed (principle of the counter-current).

A single distillation is usually insufficient for the complete elimination of all gaseous and solid constituents. For this purpose the operation must be repeated in an apparatus of platinum with a condensing coil of the same metal or of pure tin, and only the middle fraction collected.

An excellent criterion for the purity of water is to be found in the measurement of its electrical resistance. Perfectly pure water conducts the electric current scarcely at all. KOHLRAUSCH found its conductivity at 18° to be  $k = 0.04 \times 10^{-6}$ , taking as a unit the conductivity of a body a

column of which 1 cm. long and 1 cm. square in cross-section has a resistance of 1 ohm. The slightest traces of salts or even contact with the atmosphere cause a marked increase in its conductivity.

PHYSICAL PROPERTIES.

16. Water at ordinary temperatures is an odorless, tasteless liquid, showing no color in thin layers. On looking through a layer 26 meters thick, SPRING observed a pure dark-blue color. The thermometer-scale of CELSIUS is fixed according to the physical constants of water, its freezing-point being called 0° and its boiling-point at 760 mm. pressure 100°. The freezing- and boiling-points are dependent on the pressure. Water possesses the very uncommon property of having a maximum of density (minimum of volume) at a definite temperature. The volume of almost all other substances increases with rising temperature, but here it diminishes up to 3.945°, above which temperature water expands as heating continues. In the following short table its volume and specific gravity are given for a few different temperatures:

Temp.	Volume.	Sp. G.	Temp.	Volume.	Sp. G.
0	1.000122	0.999878	5	1.000008	0.999992
1	1.000067	0.999933	6	1.000031	0.999969
2	1.000028	0.999972	8	1.000118	0.999882
3	1.000007	0.999993	10	1.000261	0.999739
4	1.000000	1.000000	20	1.001730	0.998270

During the transformation of water to ice the volume increases considerably. One vol. water at 0° yields 1.09082 vol. ice of the same temperature.

The specific heat of water is greater than that of a vast majority of other substances. Its latent heat of fusion is 79 Cal., its latent heat of vaporization 536 Cal. Water is extensively used as a solvent. Numerous substances dissolve in it to a greater or less degree. There are many liquid substances that mix with water in all proportions, and many, also, which do not. (See § 7.)

The remarkable physical properties of water play a very important rôle in nature. As this subject is extensively discussed in physics, meteorology and geology, we can pass over it here with a brief summary. The marked increase of volume during the transformation of water into ice, as a result of which the specific gravity becomes less, is the reason why ice floats and

the water below remains liquid. The temperature of the deepest layers of water very seldom gets lower than  $4^{\circ}$  C., for, when a layer reaches this temperature, it is at the point of greatest density and therefore sinks to greater depths, where it is protected from farther cooling by the poor conductivity of the upper layers. These two phenomena together prevent the entire freezing of the rivers and seas in winter to a solid mass of ice, which would necessarily take place if ice were denser than water and the maximum density point of water were not above  $0^{\circ}$ . The fact that water freezes merely at the surface not only makes the existence of water animals possible, but is also of very great influence on the climate. If every body of water froze solid in winter, the heat of summer would be insufficient to melt all this ice, the latent heat of fusion and the heat capacity of water being so great. In our present temperate zone there would be a climate like that of the polar regions, and a large part of Europe would therefore be uninhabitable.

The expansion of water on freezing is moreover a very important factor in the disintegration of rocks. During rains, etc., the water percolates into the cracks of the rocks and, if it freezes, the force with which it expands is so great that the cracks are gradually widened, until the rock at last falls to pieces.

Then, too, as a solvent, water affects the minerals in various ways. In this respect it is likewise a very substantial geological factor.

#### NATURAL WATER.

17. Water, as it occurs in nature, is by no means chemically pure. It may contain solid matter in suspension as well as substances, either solid or gaseous, in solution. The purest natural water is *rain-water*. This has really passed through a natural process of distillation, the water on the earth's surface being vaporized by the sun's heat and condensed again by contact with colder portions of air, whereupon it falls in the form of rain. Nevertheless it contains dust-particles (in large cities more, of course, than in the country) and gases from the air, as well as traces of ammonium salts.

*Spring-* and *well-waters* contain in 10,000 parts about 1–20 parts solid matter, consisting largely of lime-salts. Well-water that contains much lime is called *hard* (§ 259). It also contains some carbonic acid and air in solution, both of which give it its refreshing taste; distilled water tastes flat.

Natural water is used extensively for drinking purposes. When it comes out of a soil that is contaminated by decaying organic matter, as is the case in many large cities, it is injurious to health, principally on account



of the presence of bacteria. It can be freed from these by filtration through a PASTEUR-CHAMBERLAND porcelain filter (Fig. 8).

This consists essentially of a hollow cylinder of porous porcelain (called a "candle") *A*, through whose walls the water is forced by its own pressure. The lower end of the candle opens into the exit tube.

In large cities it has been found much more practicable to purify the well- or river-water at the central station and to pipe it thence to the various houses. Epidemic diseases have really decreased remarkably since the introduction of this method.

A water which contains so many substances in solution that it has a definite taste or a therapeutic effect is called a *mineral water*. There are very many kinds of these, differing according to the amount and kind of dissolved matter they contain. We distinguish between saline waters containing common salt, bitter waters with magnesium salts, sulphurous waters with sulphuretted hydrogen, carbonated waters with carbonic acid, chalybeate waters with iron, and many others. Detailed analyses of the mineral waters of numerous watering-places are accessible in works on balneology.

*Sea-water* contains about 3% of salts, of which 2.7% is common salt. A large number of elements, viz., about thirty, have been found in sea-water, although the most of them exist there only in extremely small quantities.

It was stated above (§ 16) that pure water is blue. The color of the rivers, lakes and seas varies, however, through many nuances from pure blue to brown. This variation is due principally to the presence of more or less brownish-yellow humous (marshy) substances or an extremely fine floating slime. Both conditions can produce a brownish-yellow color. It is easily seen how the combination of blue and yellow or brown may bring about the various blue, green or brown tints in natural waters.

#### COMPOSITION OF WATER.

**18. Decomposition.** It was stated above that water can be obtained by direct combination of hydrogen and oxygen; inversely, it can be decomposed into these same elements.

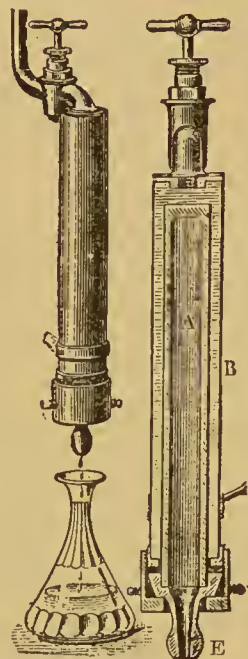


FIG. 8.—PASTEUR-CHAMBERLAND FILTER.

In the flask *A* (Fig. 9) some water is heated till it boils vigorously. A strong electric current is then sent through the wire *a c b*, so that the fine platinum wire *c* glows intensely. This heat partially decomposes the water vapor into hydrogen and oxygen, which pass out through the tube *d* and are collected in the cylinder *C*. This gas mixture is nothing but the explosive mixture (§ 13) of hydrogen and oxygen, as can be easily proven by applying a flame.

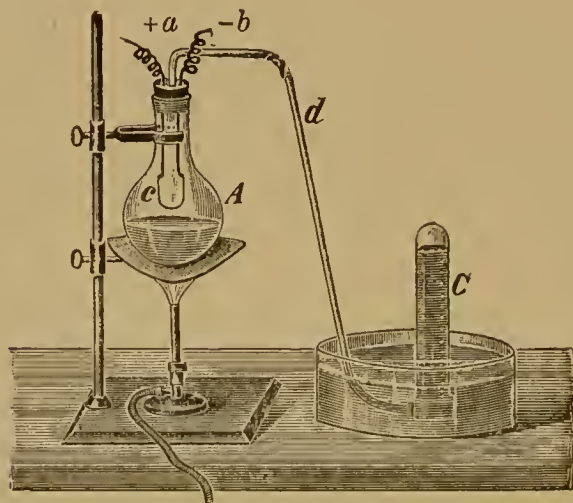


FIG. 9.—DECOMPOSITION OF WATER BY GLOWING PLATINUM.

Many metals decompose water on contact, the hydrogen being set free and the metal uniting with the oxygen. Potassium and sodium effect this decomposition at ordinary temperatures (§ 11); iron, zinc, and other metals require a higher temperature, iron, e.g. acting at red heat.

19. Let us now study the quantitative composition of water, i.e. determine the relative amounts of hydrogen and oxygen present. For this purpose both the analytical and synthetical methods can be used.

(a) *The Analytical Method.*—When an electric current is passed through water to which has been added a little sulphuric acid, the water is decomposed. If the gases evolved at the electrodes are collected separately, it is found that for every 1 vol. oxygen 2 vols. hydrogen are given off. A suitable apparatus for this experiment is shown in Fig. 10.

Since 1 liter of hydrogen weighs 0.0899 g. and 1 liter of oxygen weighs 1.4296 g., both at  $0^{\circ}$  and 760 mm. pressure, the weights of 2 vols. hydrogen and 1 vol. oxygen must bear to each other the ratio of  $2 \times 0.0899 : 1.4296$ , or 1 : 7.943.

(b) *The Synthetical Method.*—As early as 1820 the reduction of copper oxide by hydrogen was employed for this purpose by BERZELIUS; in 1834, also, by DUMAS and STAS. A weighed amount of carefully dried copper oxide is heated in a current of hydrogen and water is formed, which is collected and weighed. The weight of the oxygen given up by the copper oxide is found from the difference between the weight of the copper oxide used and that of the resulting copper. The weight of the hydrogen contained in the water collected is therefore equal to the difference in weight of water and oxygen.

The apparatus used for this experiment is represented in Fig. 11. In *A* the hydrogen is generated from zinc and dilute sulphuric



FIG. 10.—DECOMPOSITION OF WATER BY THE ELECTRIC CURRENT.

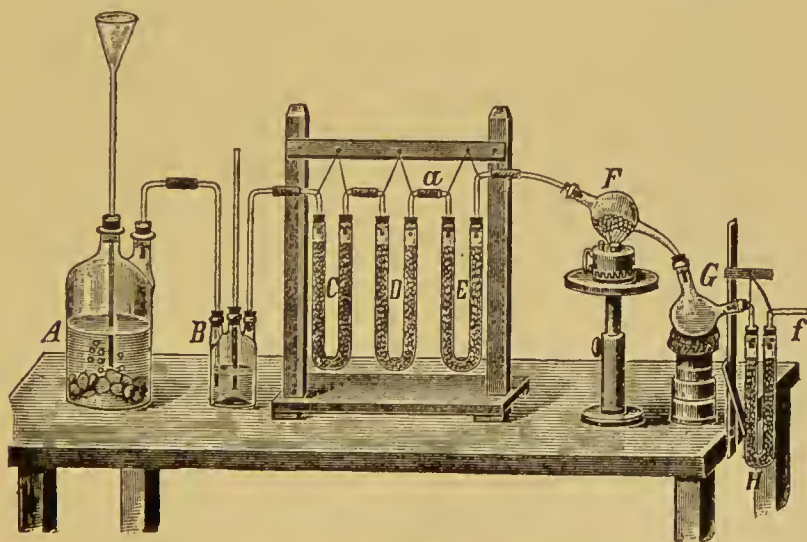


FIG. 11 --SYNTHESIS OF WATER AFTER DUMAS AND STAS.

acid. It is then passed through the permanganate solution in the wash-bottle *B* to free it from impurities, and also through the U-tubes *C*, *D* and *E*, containing calcium chloride, sulphuric acid and phosphorus pentoxide, respectively, for drying it. In *F* is placed

the copper oxide, which is carefully weighed together with the tube. The water that forms is condensed in *G*, the U-tube *H* being attached to absorb any escaping water vapor. At the completion of the experiment, *F*, with its contents, is again weighed, likewise *G* and *H*; the differences in weight indicate the amount of water formed. DUMAS and STAS found in this way that 100 parts (by weight) of water consist of 11.136 parts of hydrogen and 88.864 parts of oxygen, or, in other words, that the mass-ratio of these elements is 1 : 7.980, a relation which agrees with that obtained in (*a*) within the range of the unavoidable experimental error.

Another synthetical method, which is especially adapted to the lecture-table, consists in mixing hydrogen and oxygen and determining in what volume-ratio these gases unite. For this purpose an apparatus (Fig. 12) described by HOFMANN is best employed.

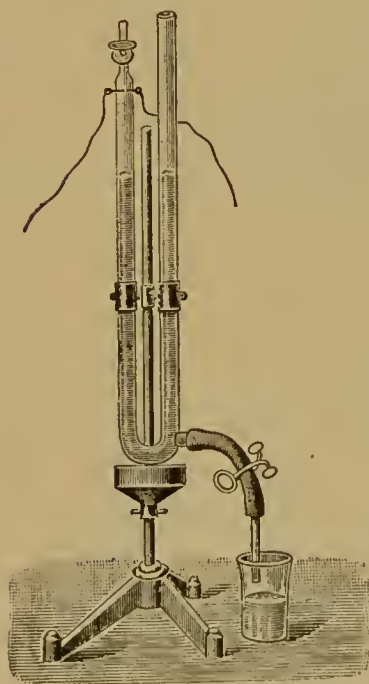


FIG. 12.—HOFMANN'S APPARATUS FOR THE SYNTHESIS OF WATER.

Hydrogen and oxygen in different proportions by volume are introduced into the arm of the U-tube, which can be closed by a stop-cock at the top; the cock is thereupon closed and the open arm tightly stoppered with a cork. The mixture is then exploded by an induction spark, the volume of air enclosed on the other side acting as a cushion to moderate the severe shock on the mercury, which might otherwise break the apparatus. It is found that *only* when the volumes of hydrogen and oxygen bear to each other the ratio 2:1 does the *entire* gas mixture disappear, a slight coating of tiny drops of water appearing in its place on the inside of the glass. In case more hydrogen or more oxygen than the ratio calls for is let into the tube, the excess is found to remain after the explosion.

From these experiments, analytical and synthetical, it follows that *water has a constant composition*; it consists of 2 volumes of hydrogen and 1 volume of oxygen, or of 1 part, by weight, of hydrogen to 7.943 parts of oxygen.

## COMPOUNDS AND MIXTURES.

20. In water we have become acquainted with a substance which is different in many and important respects from the elements of which it is composed. We have farther seen that the elements in it bear to each other a fixed relation by weight. Such substances are known in very large number. Copper oxide, mercury oxide, sulphuric acid, potassium chlorate, common salt, soda and many others already mentioned belong to this class. In each of these, no matter how obtained, we discover by analysis or synthesis a definite proportion between the elements composing it. Such substances are called **compounds**.

In addition to the characteristics mentioned—difference of properties from those of the elements and constant composition—we find that the compounds also have constant physical properties. Under the same pressure water always has the same melting-point and the same boiling-point, in whatsoever way it may have been obtained; salt always crystallizes in the same crystal form; soda, at a definite temperature, always requires the same amount of water for solution, etc.

When elements or compounds are brought together without any chemical action on each other taking place, we have a **mixture** of these elements or compounds. The number of possible mixtures is, of course, unlimited. They are distinguished from compounds by the following characteristics:

In a mixture the properties of the components reappear in many and important respects. Gunpowder, for example, is a mixture of sulphur, charcoal and saltpetre. The latter is soluble in water; sulphur dissolves in carbon bisulphide; charcoal is insoluble in both. These properties are still evident in the constituents of gunpowder. In a mixture of sulphur and iron-filings one can detect with a microscope the yellow grains of sulphur and the black particles of iron. The iron can be drawn out with a magnet; the sulphur dissolved out by carbon bisulphide. If, however, a mixture of 7 parts iron and 4 parts sulphur is heated, a glow passes through the powder and a compound of both—iron sulphide—is formed, whose properties are entirely different from those of its elements. It is non-magnetic, insoluble in carbon bisulphide and under the microscope only a homogeneous scoriaceous mass is seen. The constituents of a mix-

ture, since they still preserve their properties, can often be separated from each other by *mechanical means*, e.g. by the use of microscope and tweezers, by sifting, by treatment with solvents, by washing, etc.

In a mixture the ratio of the constituents can vary in all proportions. There are, for example, many sorts of gunpowder, distinguished from each other by the proportions in which their constituents are mixed. When 1 part sulphur and 100 parts iron, or, on the other hand, 1 part iron and 100 parts sulphur are mixed, we have in either case a mixture of both elements, possessing hardly the same, but at least analogous, properties.

Moreover, a mixture often has no constant physical properties. Water has a constant boiling-point; the boiling-point of a mixture of benzene and turpentine, however, rises gradually as the more volatile component, benzene, distills off. The melting-point of sulphur is constant and can be accurately determined; that of a mixture of tin and lead differs according to the proportion of the elements and is in many proportions not at all sharp, there being only a softening instead of real fusion.

In the examples cited here the distinction between a compound and a mixture is well marked. There are, however, other instances where this is not the case and where it is therefore very difficult to know whether one is dealing with a compound or a mixture. We shall meet with many examples of this later. There is, however, *one* way whereby a compound can be distinguished from a mixture, viz., by ascertaining whether or not the substance, prepared in different ways, has a constant composition.

### PHENOMENA ACCOMPANYING THE FORMATION OR DECOMPOSITION OF A COMPOUND.

The most common phenomenon of this sort is an elevation or depression of temperature, i.e. an evolution or absorption of heat (calorific effect). Sometimes the rise of temperature is so great that light is produced. A decomposition or a combination can be so violent that it causes an explosion. In other instances electricity may be produced by chemical action. All these facts may be comprised in this statement: *Chemical action results in a change in the energy-supply of the reacting substances.*

### EXPLANATION OF THE CONSTANT COMPOSITION OF COMPOUNDS.—ATOMIC THEORY.

21. It was stated that constant composition is the distinctive characteristic of a chemical compound. This **Law of Constant Composition** (definite proportions) was finally established by PROUST in the beginning of the nineteenth century, and at about the same time (1807) DALTON offered an explanation of it which is still accepted and may be considered as the foundation of theoretical chemistry.

Matter can be thought to be infinitely divisible; according to human conception, the smallest particle that can really be obtained is still capable of division into an infinite number of others. Nevertheless even the ancients were of the opinion that there must be somewhere a limit to the divisibility and that one must finally arrive at particles incapable of farther division, the **atoms**.

In the fifth century B.C. there existed a school of philosophy, that of the *Eleatics* (so-called from the city of ELEA), whose most prominent representative was PARMENIDES. He taught that everything that exists cannot be otherwise conceived than as unchangeable; transformation of the existent, which was thought to have never originated and to be at the same time unalterable, was held by them to be inconceivable. These theses they regarded in a certain sense as axioms, i.e. statements of truths which are accepted without proof. Daily experience teaches one nevertheless that transformation does occur in that which exists, a fact that led them to suppose that everything observed by men is merely appearance.

Three theories were proposed in the same century which aim to form a bridge between the doctrine of the unalterable existent and the experience that points toward continuous change. These theories originated with EMPEDOCLES, ANAXAGORAS, and the *Atomists*, LEUCIPPUS and DEMOCRITES. The immutability of the existent is disposed of by ascribing it to extremely small unchangeable and indestructible particles; every change is thought to depend on the movement of these smallest integral particles towards or away from each other. EMPEDOCLES and ANAXAGORAS assume in this connection an infinite divisibility; the *Atomists*, on the contrary, regard the world as built up of indivisible particles, atoms, all of which consist of the same primordial substance but differ in form and size.

Now DALTON has used this conception of the ancients regarding the atom to explain the fact that the combining weights are constant. The atoms of the various elements, he assumes, have different weights; the atoms of the *same* element are alike in weight. A compound of two elements is therefore produced by the associa-

tion of atoms of these elements. Such a combination of two or more atoms is called a **molecule**. It is obvious that these suppositions lead directly to the *law of constant proportions*; for, if copper oxide is formed by an atom of copper uniting with an atom of oxygen to make a molecule of copper oxide, its composition must, according to the above hypothesis, be constant. DALTON deduced another conclusion from his hypothesis and confirmed the same experimentally. He observed that oxygen unites not only with *one* very definite amount of nitrogen oxide, but also with twice as much, not, however, with any intermediate amount. He also showed by the investigation of marsh gas and olefiant gas, both of which are made up of only carbon and hydrogen, that the former contains twice as much hydrogen to a certain weight of carbon as the latter. It is readily seen how such observations can be explained on the basis of the atomic theory; in one case 1 atom of carbon is in combination with  $n$  atoms of hydrogen; in the other with  $2n$  atoms.

The observations of DALTON were subsequently confirmed and extended, especially by BERZELIUS. The following statement is therefore now accepted as a law: *When two elements combine to form more than one compound, the different weights of the one element which unite with one and the same weight of the other element bear a simple ratio to each other.* This is the **Law of Multiple Proportions**.

**22.** The absolute weight of the atoms is not exactly known. It is so small that no one has as yet succeeded in determining either the size or the weight of the atoms (or of the molecules) except approximately.

The following data may give an idea of the real amounts :

1. Many substances, e.g. musk and certain organic sulphur compounds, possess an extremely powerful odor. If a bottle containing such a substance is opened in a room for a few moments, the odor can soon be detected throughout the entire room; nevertheless, even a sensitive balance fails to show any perceptible decrease in the weight of the bottle. The extremely small amount of the substance which evaporated contains, therefore, such a large number of molecules that when these are distributed in a relatively large space, the odor can be detected in all parts.

2. FARADAY prepared gold-leaf not more than  $0.5 \times 10^{-6}$  mm. thick. Considering that this thickness must represent the diameter of at least one atom of gold, it is plain that the actual diameter must be under the above limit.

3. It is assumed that the molecules of a gas are free to move in all



directions. As a result, the molecules must encounter each other very frequently. Moreover the length of the free path through which the gas molecules may move without collision depends on their size. This free path can be calculated, as is shown in physics, from measurements of the diffusion, heat-conductivity and internal friction of the gases. When it is known, we can estimate the size of the molecules. Thus, VAN DER WAALS was able to arrive at the following approximations: The number of molecules in 1 mm.<sup>3</sup> air at 0° and 760 mm. Hg. pressure is represented by a number of seventeen figures; 1 mm.<sup>3</sup> air weighs, however, only  $1.3 \times 10^{-6}$  g. The weight of one atom of hydrogen in milligrams was calculated to be a number of the  $10^{-21}$  order.

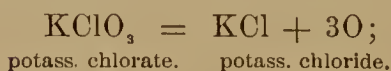
### CHEMICAL SYMBOLS.

23. The absolute weight of the atoms is thus only approximately known. Nevertheless, their **relative weights**, i.e. the weights of the atoms of the other elements when that of a *certain* element is *arbitrarily* fixed, have been determined in a variety of ways. These relative weights, which are known as **atomic weights**, are expressed by symbols, that were introduced by BERZELIUS and are of great convenience in the representation of compounds and the formulating of chemical processes. Such a symbol expresses not only what element one is dealing with, but also the relative weight of an atom. If the atomic weight of copper is 63.3 and that of oxygen 16, the symbol Cu indicates 63.3 parts by weight of copper, the symbol O 16 parts by weight of oxygen. It has been determined that in copper oxide one atom of copper is combined with one atom of oxygen; copper oxide is therefore represented by the formula CuO, which expresses, first, that we are dealing with a compound of copper and oxygen, and, second, that 1 atom (63.3 parts by weight) of copper is united in it to 1 atom (16 parts by weight) of oxygen. Many compounds contain several atoms of the same element. This is indicated by placing the proper figure to the right of and below the symbol. Sulphuric acid, for example, contains 2 atoms of hydrogen (H), 1 atom of sulphur (S) and 4 atoms of oxygen (O) in the molecule. Its formula is, therefore, H<sub>2</sub>SO<sub>4</sub>.

Chemical actions can be very simply represented by the use of these formulæ; thus, the decomposition of mercuric oxide into oxygen and mercury by



that of potassium chlorate into oxygen and potassium chloride by



the generation of hydrogen from zinc and sulphuric acid by



In such equations the same atoms and the same number of each must appear on both sides, in accordance with the principle of the Indestructibility of Matter.

Besides the atomic weights, we quite frequently use equivalent weights. These are the weights of the elements which combine with a unit amount of a certain standard element. One part of hydrogen combines, for instance, with 35.5 parts of chlorine and with 8 parts of oxygen. These amounts of hydrogen, chlorine and oxygen are equivalent to each other. The atomic weight is either equal to the equivalent weight or a multiple of the same.

### STOICHIOMETRICAL CALCULATIONS.

24. If the formulæ of the compounds are known—the means of ascertaining these will be discussed in detail later—and the atomic weights of the elements composing them also known, it is very easy to calculate the weights that enter into reaction in all chemical changes. A couple of examples may serve to make this clear.

1. It is required to know *how many liters of oxygen at 0° and 760 mm. pressure can be obtained by heating 1 kilogram of mercuric oxide.*

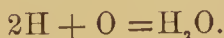
The atomic weight of mercury is 200, that of oxygen is 16; HgO is therefore 200 + 16. Out of these 216 parts by weight of mercuric oxide 16 parts of oxygen can be obtained by heating, i.e. from 1 kilo (= 1000 g.) can be obtained  $\frac{1000 \times 16}{216} = 74.07$  g. Since 1 l. oxygen at 0° and 760 mm. pressure weighs 1.4296 g., 74.07 g. occupy a volume of  $\frac{74.07}{1.4296} = 51.8$  l.

2. *How much water can be formed from the hydrogen obtained by the interaction of 1 kg. zinc and the corresponding amount of sulphuric acid?*

The reaction of zinc and sulphuric acid is expressed by the equation



and the combustion of hydrogen to form water by the equation



From these equations it follows that the hydrogen formed by the action of 1 atom of zinc yields 1 molecule of water. For every atom of zinc we obtain, therefore, 1 molecule of water. The atomic weight of zinc is 65, the molecular weight of water 18; therefore 65 parts of zinc correspond to 18 parts of water. 1 kg. zinc must yield  $\frac{1000 \times 18}{65} = 276.9$  g.

3. How many grams of potassium chlorate are necessary to produce enough oxygen to oxidize 500 g. copper to copper oxide?

The reactions concerned are



Hence 3 atoms of copper can be oxidized with the oxygen derived from 1 molecule of potassium chlorate. For every 3 atoms of copper 1 molecule of potassium chlorate must be consumed. The molecular weight of the latter substance is  $39 + 35.5 + 3 \times 16 = 122.5$ ; the atomic weight of copper is 63; for every 63 parts of copper  $\frac{122.5}{3} = 40.8$  g. potassium chlorate are therefore required.

Hence 500 g. copper require  $\frac{500 \times 40.8}{63} = 323.8$  g. potassium chlorate.

In most chemical computations *gram-molecules* are employed, these being the molecular weights of the substances in grams. The abbreviation *mol* has been suggested by OSTWALD for this term. Thus "1 mol" copper oxide means  $63 + 16 = 79$  grams of it.

The molecular weight in milligrams is called a *millimol*. In the same way we may speak of a *kilomol*, etc.

It is now customary to take the atomic weight of oxygen as 16.

The atomic weights of the remaining elements then have the values that are given in the following table :

TABLE OF ATOMIC WEIGHTS.

Atom.	Symbol.	Atomic Weight.	Atom.	Symbol.	Atomic Weight.
Aluminium.....	Al	27.1	Neodymium.....	Nd	143.6
Antimony.....	Sb	120	Neon.....	Ne	20
Argon.....	A	40	Nickel.....	Ni	58.7
Arsenic.....	As	75	Niobium.....	Nb	94
Barium.....	Ba	137.4	Nitrogen.....	N	14.04
Beryllium.....	Be	9.1	Osmium.....	Os	191
Bismuth.....	Bi	208.5	Oxygen.....	O	16.00
Boron.....	B	11	Palladium.....	Pd	106
Bromine.....	Br	79.96	Phosphorus.....	P	31.0
Cadmium.....	Cd	112.4	Platinum.....	Pt	194.8
Cæsium.....	Cs	133	Potassium.....	K	39.15
Calcium.....	Ca	40	Praseodymium..	Pr	140.5
Carbon.....	C	12.00	Rhodium.....	Rh	103.0
Cerium.....	Ce	140	Rubidium.....	Rb	85.4
Chlorine.....	Cl	35.45	Ruthenium.....	Ru	101.7
Chromium.....	Cr	52.1	Samarium.....	Sa	150
Cobalt.....	Co	59.0	Scandium.....	Sc	44.1
Copper.....	Cu	63.6	Selenium.....	Se	79.1
Erbium.....	Er	166	Silicon.....	Si	28.4
Fluorine.....	F	19	Silver.....	Ag	107.93
Gallium.....	Ga	70	Sodium.....	Na	23.05
Germanium.....	Ge	72	Strontium.....	Sr	87.6
Gold.....	Au	197.2	Sulphur.....	S	32.06
Helium.....	He	4	Tantalum.....	Ta	183
Hydrogen.....	H	1.01	Tellurium.....	Te	127
Indium.....	In	114	Thallium.....	Tl	204.1
Iodine.....	I	126.85	Thorium.....	Th	232.5
Iridium.....	Ir	193.0	Tin.....	Sn	118.5
Iron.....	Fe	56.0	Titanium.....	Ti	48.1
Krypton.....	Kr	81.6	Tungsten.....	W	184
Lanthanum.....	La	138	Uranium.....	U	239.5
Lead.....	Pb	206.9	Vanadium.....	V	51.2
Lithium.....	Li	7.03	Xenon.....	X	128
Magnesium.....	Mg	24.36	Ytterbium.....	Yb	173
Manganese.....	Mn	55.0	Yttrium.....	Y	89
Mercury.....	Hg	200.3	Zinc.....	Zn	65.4
Molybdenum....	Mo	96.0	Zirconium.....	Zr	90.7

The atomic weights in the above table are carried out to as many decimal places as may be accepted with certainty. For many purposes it is sufficient to use round numbers, such as N = 14, Br = 80, etc.

The acceptance of 16 as the atomic weight of oxygen has a historic reason. For a long time hydrogen was taken to be 1; it was believed that the ratio of the atomic weights of hydrogen and oxygen was 1:16. Inasmuch as the atomic weights of most elements are determined from the com-

position of their oxygen compounds, the basis is really  $O = 16$  and not  $H = 1$ . This made no difference, so long as the proportion  $H : O = 1 : 16$  was considered accurate. Even when the ratio was later found to be a different one (according to the recent investigations of EDWARD W. MORLEY the ratio  $1 : 15.88$  may be regarded as quite accurately determined), it was still the simplest plan to preserve  $O = 16$  as the basis, since a change would necessitate a complete recalculation of all the atomic weights, and this necessity would moreover recur as often as a new refinement of methods of investigation brought about a change in the ratio  $H : O$ .

### CHLORINE.

25. Chlorine is a greenish-yellow gas (hence its name;  $\chi\lambda\omega\rho\acute{o}\varsigma$  = greenish yellow), which does not occur free in nature, since it acts upon the most diverse substances at ordinary temperatures. In compounds, however, it occurs quite extensively. Common table-salt is a compound of sodium and chlorine. Various other metallic chlorides are also met with in nature.

Chlorine-gas can be obtained by the *direct* decomposition of certain chlorine compounds; thus:

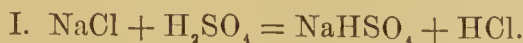
1. By the electrolysis of hydrochloric, or muriatic, acid (i.e. a solution of hydrogen chloride,  $HCl$ , in water). Chlorine is given off at the positive pole (anode), hydrogen at the negative (cathode).

The *indirect* decomposition of its compounds offers, as in the case of hydrogen (§ 11), the *most practicable* methods of obtaining the element. They are all based on the oxidation of the hydrogen of hydrochloric acid, whereby water is formed and chlorine liberated.

2. Commercially, as well as in the laboratory, manganese dioxide,  $MnO_2$ , is frequently used as the oxidizing agent:



It is very often convenient to generate the hydrochloric acid from salt and sulphuric acid in the same vessel with the manganese dioxide. The two reactions thus proceed simultaneously:



3. Other commonly used oxidizing agents are chloride of lime and potassium bichromate, e.g.:



4. The oxygen of the air can also serve as the oxidizing agent when a catalyzer is present. For this purpose a mixture of air and hydrogen chloride is passed over porous bricks at 370–400°, which are soaked with copper sulphate solution:



This method, which is known as the *Deacon process*, is used commercially. The copper sulphate is here the catalyzer.

At the temperature of 370°–400° there is practically no reaction between oxygen and hydrogen chloride without the catalyzer. That there must nevertheless be a reaction, although a very slow one, can be demonstrated by the same reasoning as in § 13. The catalyzer therefore does not cause a reaction, but only accelerates it. OSTWALD compares its action to that of oil on the axles of a machine which move with very great friction. When oiled, the machine will go much faster, notwithstanding that the force of the spring (here the energy of the chemical reaction) has not changed. A farther point in the analogy is that the oil is not consumed.

**26. Physical Properties.**—Chlorine is yellowish green and has a disagreeable odor. Its specific gravity is 2.45, taking air as unity, or 35.45, based on O = 16. 1 l. chlorine weighs, therefore, 3.208 g. at 0° and 760 mm. pressure. At –34° it becomes liquid under ordinary pressure; at –102° it solidifies and crystallizes. Its critical temperature is 146°. Liquid and solid chlorine are yellow. Chlorine gas dissolves in about one-half its volume of water. The aqueous solution bears the name “chlorine water.” It can, therefore, not be collected over water, but a saturated salt-solution may be used, in which it is only slightly soluble. The most convenient way to fill a vessel with it is by displacement of air, the gas being conducted to the bottom, where it remains and drives out the air above, because the chlorine is denser.

**27. Chemical Properties.**—Even at ordinary temperatures, chlorine combines with many elements and acts on many compounds. If perfectly pure chlorine is mixed with an equal volume of hydrogen, the two unite in direct sunlight, causing an explosion. If the chlorine is impure or the sunlight diffused, combination occurs

slowly. When a hydrogen flame is introduced into chlorine gas, it continues to burn, with the formation of hydrogen chloride. Many metals combine with chlorine with the evolution of light, e.g. copper (in the form of imitation gold-leaf), finely powdered antimony, molten sodium, etc. The precious metals are in general quite resistive to chemical action. They are, however, attacked by chlorine and changed to chlorides, i.e. chlorine compounds. Gold, for instance, dissolves in chlorine water, forming gold chloride.

Chlorine also unites readily with many non-metals, e.g. phosphorus, which burns in it with a pale flame to phosphorus chloride.

The tendency of chlorine to unite with hydrogen—its so-called *chemical attraction*, or *affinity*, for the latter—is so strong that chlorine abstracts the hydrogen from many hydrogen compounds in order to combine with it. A strip of paper dipped in turpentine burns with a sooty flame when introduced into an atmosphere of chlorine; the chlorine unites with the hydrogen of the turpentine and sets the carbon free. A burning candle continues to burn in chlorine, depositing soot (carbon) and forming hydrogen chloride. If sulphuretted hydrogen gas,  $H_2S$ , is passed into chlorine water, hydrochloric acid and sulphur are formed.

Water is also decomposed by chlorine, oxygen being liberated,



This reaction takes place under the influence of sunlight, but proceeds very slowly. A suitable apparatus for its demonstration is pictured in Fig. 13. An inverted retort is filled with dilute chlorine water and exposed to the sunlight. After a few days a bubble of gas collects at the top of the retort, and, on investigation with a glowing splinter, it is found to be oxygen.

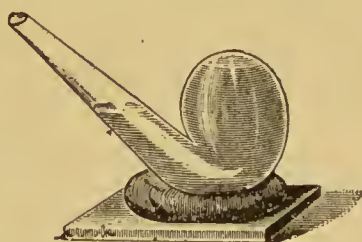


FIG. 13. — SLOW DECOMPOSITION OF WATER BY CHLORINE.

Upon this decomposition of water depends the *bleaching and disinfecting action* of chlorine and those substances which generate chlorine. In bleaching, the coloring matters—usually of an organic nature—are oxidized by oxygen to colorless substances. Bacteria are killed by oxidation. Ordinary atmospheric oxygen does not produce these effects. Litmus, for instance, which is rapidly decolorized in moist chlorine gas, is totally unaf-

fect by the air. The particularly energetic action of the oxygen that is produced from water by chlorine is explained by assuming that it exists in an atomic condition, the *status nascens*, regarding which more will be said later (§ 38). Perfectly dry chlorine has no bleaching power.

If water is saturated with chlorine at 0°, crystals are deposited, of the composition  $\text{Cl}_2 + 8\text{H}_2\text{O}$ , **chlorine hydrate**. At a higher temperature these are wholly decomposed into chlorine and water.

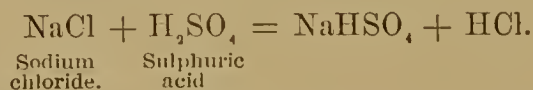
#### HYDROCHLORIC ACID, OR HYDROGEN CHLORIDE, HCl.

28. Hydrochloric acid, of the formula HCl (§ 31), is a gas, occurring in nature in the free state, e.g. in the gases of some volcanoes. It forms an important, although small, part of the gastric juice of man and other animals.

Some of its *methods of formation* have been already given (§ 28), viz., by direct synthesis from its elements, and also by the action of chlorine on hydrogen compounds. Moreover, it can also result from the action of hydrogen on some chlorine compounds, e.g. silver chloride,  $\text{AgCl}$ , and lead chloride,  $\text{PbCl}_2$ , when heated in a current of hydrogen, yield metal and hydrochloric acid.



The ordinary method of preparation is by the action of a chlorine compound on a hydrogen compound, viz., that of salt (sodium chloride) on concentrated sulphuric acid.



This method is employed technically as well as in the laboratory.

The above reaction takes place at ordinary temperatures. If the sulphuric acid is to be completely used up, i.e. if all the hydrogen of the sulphuric acid is to go off with the chlorine of the salt as hydrochloric acid, the temperature of the reaction must be raised (*cf.* also § 226):



29. *Physical Properties*.—Hydrogen chloride is a colorless gas with a pungent odor. Its critical temperature is + 52.3°; the critical pressure 86 atmospheres. Liquid hydrogen chloride boils



at  $-83.7^{\circ}$ ; the solid melts at  $-111.1^{\circ}$ . Sp. G. of the gas = 1.2696 (air = 1); 1 l. HCl at  $0^{\circ}$  and 760 mm. pressure weighs, therefore, 1.6533 g. The gas fumes strongly in the air, forming a cloud with the moisture of the air. It is very soluble in water, 1 vol. water at  $0^{\circ}$  being able to absorb 503 vols. HCl gas. The aqueous solution of the gas is called "hydrochloric acid,"\* also *muratic acid*. It is manufactured commercially on a large scale (§226). Hydrochloric acid is employed almost exclusively in the form of this aqueous solution. A solution saturated at  $15^{\circ}$  contains 42.9% HCl and has the specific gravity 1.212; it fumes vigorously in the air. The ordinary pure "concentrated" or "fuming" muriatic acid of commerce usually has a specific gravity of 1.19 and contains about 38% HCl.

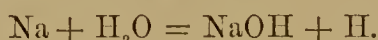
Hydrogen chloride does not obey the law of HENRY (§ 9) in its behavior towards water; that is, its solubility in this liquid is not at all proportional to its pressure. The larger part of it is absorbed in water without reference to the pressure, and an augmentation of the latter causes only a small increase in the solubility. Such conduct indicates that a change in the compound has occurred; just what this change consists in we shall soon have occasion to consider. When hydrogen chloride is led into water till the solution becomes saturated, most of it undergoes this change; only a relatively small part exists in solution as unchanged hydrogen chloride, and it is this part only that obeys HENRY'S law. This explains why the amount dissolved increases much more slowly than the pressure.

30. The *chemical properties* of hydrogen chloride are found to be quite different when it is in a perfectly dry condition, e.g. condensed to a liquid, than when it is dissolved in water. In the former case it does not act on metals nor change the color of blue litmus. In the latter case just the contrary is true. Zinc, iron, and other metals, when dipped in the aqueous solution of hydrogen chloride, are vigorously attacked, hydrogen being given off. Blue litmus is turned red by the solution. Moreover, even dilute solutions taste sour. Now, there are a lot of substances that undergo a similar change of properties when they are brought in contact with water, and whose aqueous solutions possess about the same properties as those that are described here for hydrochloric

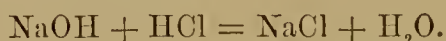
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\* The gas itself is often called "hydrochloric acid gas."

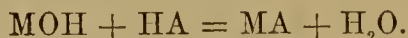
acid. The nature of this change will be discussed later on (§ 65). It should be stated here, however, that these substances have a common name. They are called **acids**. *Acids have one or more hydrogen atoms that can be replaced by metals.* The compounds of metals that are formed by such substitution are called **salts**. Salts can result not only from the direct action of metals on acids, but also from the interaction of acids and **bases**. The term "bases" includes compounds of the general type MOH, where M represents a metal. Most of them have an alkaline taste and turn red litmus blue. When sodium is dropped into water, hydrogen is generated, and a base, sodium hydroxide, is formed :



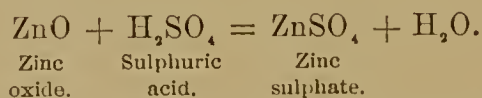
If this hydroxide is now treated with hydrochloric acid, sodium chloride and water are produced :



If we indicate an acid by the general formula AH and a base by MOH, the formation of salts from the interaction of the two may be represented thus:

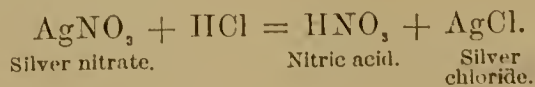


A third way of forming salts is by the action of an acid upon a metallic oxide, e.g. :



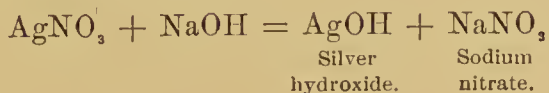
In general, the bases are built up from metals, the acids from metalloids.

When hydrochloric acid is added to a solution of a silver salt, for instance to silver nitrate, a decomposition of this salt takes place according to the equation



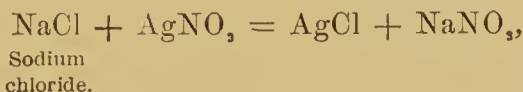
The silver chloride is insoluble, and is precipitated as a white, curdy mass. In this reaction the hydrochloric acid has liberated the nitric

acid from its salt. It is also possible to liberate a base from a salt by the addition of another base:



Such reactions are called *single*, or *simple*, *decompositions*.

Now it can also occur that two salts exchange their metals when brought together:



so that two other salts are obtained. Such a reaction between salts is called a *double decomposition*.

We shall later have occasion to study the laws governing both of these decompositions.

#### COMPOSITION OF HYDROCHLORIC ACID. LAWS OF GAY LUSSAC AND AVOGADRO.

31. The composition of hydrochloric acid is determined by the following experiments:

(a) Strong hydrochloric acid (i.e. above 23%) is subjected to electrolysis. By properly arranging the apparatus it may be seen that *equal volumes* of hydrogen and chlorine are evolved.

(b) Equal volumes of chlorine and hydrogen unite to form hydrochloric acid without leaving a remainder of either element. 2 vols. HCl are formed. Since the weight of 1 vol. Cl is 35.45 (O = 16), hydrochloric acid must consist of 1 part by weight of hydrogen combined with 35.45 parts of chlorine.

In the electrolysis of hydrochloric acid sticks of charcoal are ordinarily used because platinum, the substance employed in most other electrolyses, is attacked by chlorine. The apparatus of Fig. 10 is also impracticable, since the solubility of chlorine in water increases with rising pressure more rapidly than that of hydrogen, and equal volumes of both gases are therefore not obtained. In its place we use an apparatus suggested by LOTHAR MEYER (Fig. 14), by which the compression of the chlorine by a steadily rising column of liquid is avoided. In *A* hydrochloric acid is electrolyzed and the hydrogen and chlorine are collected in the cylinders *BB*, which are

filled with a saturated sodium chloride solution. The collected gases are thus under diminished pressure.

The combination of equal volumes of chlorine and hydrogen can be carried out in a thick-walled tube, that is filled with the gases and then exposed for a day to diffused sunlight. Since the success of the experiment requires the use of the exact proportions of chlorine and hydrogen and their absolute purity, the gas mixture is prepared by electrolysis in the dark and exposed to the action of light immediately after the tube is filled.

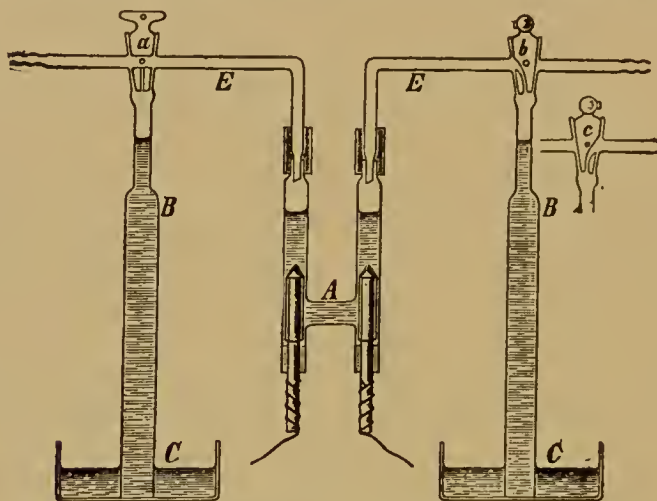


FIG. 14.—ELECTROLYSIS OF HYDROCHLORIC ACID.

The fact that hydrochloric acid gas yields a volume of hydrogen equal to half its own volume can also be shown in another way. When perfectly dry hydrogen chloride is treated with sodium amalgam—a solution of sodium in mercury—the sodium combines with the chlorine, setting hydrogen free. The volume of the latter is then found to be half as large as that of the hydrochloric acid employed.

Hydrogen and chlorine thus unite in a very simple ratio by volume (1:1) and the volume of their product also bears a very simple ratio to that of the components (2:1:1). In discussing the composition of water (§ 19) we already remarked that oxygen and hydrogen combine in a very simple ratio by volume, viz., 1:2.

By carrying out the experiment (§ 19) at a temperature above  $100^{\circ}$ , so that the steam is not condensed to water, it is also found that the volume of resulting steam is in a simple ratio to that of its components, viz., that 1 vol. O + 2 vol. H gives 2 vols.  $\text{H}_2\text{O}$ .

The following arrangement serves this purpose (Fig. 15). The explosive mixture is introduced into the closed arm *B* of the U-tube over mercury

*B* is surrounded by a glass jacket, through which the vapor of boiling amyl alcohol (generated in *A*), whose temperature is about  $130^{\circ}$ , is passing. This vapor is condensed in *C*. As soon as the gas mixture has reached this temperature, an induction spark is flashed through, and it is found that the volume of steam formed is two-thirds that of the mixture.

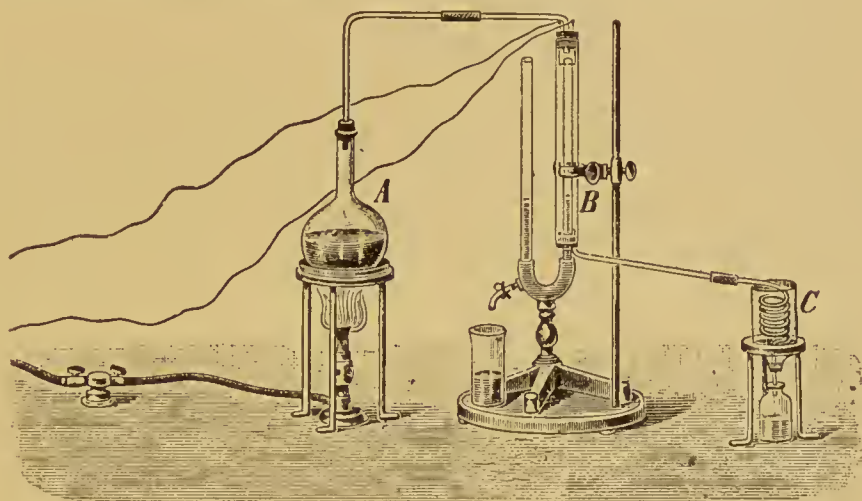


FIG. 15—DETERMINATION OF THE VOLUME-RELATIONS BETWEEN STEAM AND ITS COMPONENTS.

What was found above to be true for hydrochloric acid and for water is a general principle. *Gaseous elements combine in simple proportions by volume, and the volume of the products formed—in the gaseous state—also bears a simple ratio to that of the components.* This law was discovered by GAY LUSSAC in 1808.

This law, together with the atomic theory of DALTON, leads to important truths. In order to investigate the matter, let us assume that the formula of hydrochloric acid is  $\text{HCl}$ ; in other words, that an atom of hydrogen is in combination with an atom of chlorine. Moreover, since one volume of hydrogen unites with one volume of chlorine to form the compound, it follows from the above assumption that equal volumes of chlorine and hydrogen contain an equal number of atoms.

If the formula were otherwise, e.g.  $\text{H}_n\text{Cl}_m$ , the numbers of atoms in equal volumes of hydrogen and chlorine would be in the ratio of  $n : m$ .

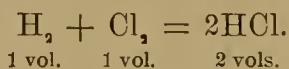
In the synthesis of water 2 volumes of hydrogen and 1 volume of oxygen yield 2 volumes of steam. If the formula of water be

$H_nO_p$ , the numbers of atoms in equal volumes of hydrogen and oxygen must bear to each other the ratio  $n : p$ .

From this it follows that a knowledge of the relation of the numbers of atoms that are present in equal gas volumes enables us to know the formulas of their compounds, provided the volume-ratio in which they unite is also known.

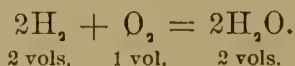
As to the number of atoms in equal gas volumes, there was at first much uncertainty. Since all gases behave exactly alike towards changes of pressure or temperature, it was reasonable to suppose that the number should be alike for all gases; but this was soon shown to be incorrect. In the synthesis of water 3 volumes (2 vols. H + 1 vol. O) give 2 volumes of steam; hence the number of atoms per unit volume must be different for steam than for the uncombined elements. However, all difficulties were overcome by a hypothesis, which AVOGADRO enunciated in 1811, to the effect that *equal volumes of all gases at the same temperature and pressure contain the same number of molecules*.

AVOGADRO further supposes that the molecules of oxygen, hydrogen, chlorine, and other elements consist of two atoms. The union of hydrogen and chlorine is then explained thus: Out of a molecule of each, two molecules of hydrochloric acid are formed:



The total number of molecules thus remains the same after the combination and, since the entire volume has suffered no change either, there must be just as many molecules present in each of the two volumes of hydrochloric acid as in each of the volumes of hydrogen and chlorine.

The combination of hydrogen and oxygen takes place thus:



Every molecule of oxygen has split up into its two atoms, and each of these unites with two hydrogen atoms. The number of water molecules becomes therefore twice as great as that of the oxygen molecules and equal to that of the hydrogen molecules; but, since the volume of steam is also double that of oxygen, there must

be in equal volumes just as many water molecules as oxygen molecules and hydrogen molecules.

32. It follows from the above that AVOGADRO'S hypothesis is of importance in two respects: (1) in furnishing us a means of ascertaining the relative weights of the molecules of gaseous substances; (2) in putting us in a position to form an idea of how many atoms there are in the molecules.

Let us examine both points more closely. As to (1): Since equal volumes of gases under the same conditions contain the same number of *molecules*, the ratio of the weights of these volumes gives us at once the ratio of the **molecular weights**. If the specific gravity of steam is 9, based on  $H = 1$ , and that of hydrochloric acid is 18.25, the ratio of the molecular weights of water and hydrochloric acid is 9:18.25. The determination of the specific gravity of gases and vapors, the **vapor density**, becomes therefore of the greatest importance to chemistry.

The specific gravity of gaseous substances is determined by weighing a flask, first empty, and then filled with the gas, observing all the precautions which are prescribed in physics for such determinations.

Methods for determining the vapor density of liquid and solid compounds at ordinary temperatures have been devised by A. W. HOFMANN and by V. MEYER, which are both rapid and convenient.

In order to calculate the vapor density (i.e. the specific gravity of a substance in the form of gas), four quantities must be known: (1) the weight of substance that is converted into vapor; (2) the volume occupied by the vapor; (3) the temperature at which the volume is measured; (4) the pressure exerted on the vapor.

The vapor density is usually determined by the method of VICTOR MEYER.

The apparatus required consists of a glass tube (Fig. 16) of about 4 mm. internal diameter in the middle, which is closed at the top with a stopper and has a wider cylindrical part of about 200 c.c. capacity below. This wider part is sealed at the bottom. Near the top a delivery-tube *A* is attached, which opens below the surface of water in *D*, under a gas-measuring tube. The apparatus is partly surrounded by a glass (or metal) jacket ending in a bulb *C*, which contains a liquid that has a higher boiling-point than the substance whose vapor-density is to be determined. This liquid is heated to boiling; the air in the apparatus of course expands; soon a point is reached at

which no more bubbles leave the delivery-tube, indicating that the air in the lower part has reached a constant temperature,—approximately that of the vapor of the boiling liquid. The graduated tube, filled with water, is now placed over the mouth of the delivery-tube, the stopper removed, a weighed quantity of the substance in question (usually in a small glass tube) dropped in and the stopper at once replaced. The substance vaporizes quickly in the hot lower part of *B*. Its vapor forces a volume of air, equal to its own, out of the apparatus, and this is collected in the graduated tube. The air in the heated part of the apparatus is at the temperature of the latter, but in the measuring-tube it takes on the temperature of the room, a fact which must be considered in the calculation. The experiment gives us therefore a volume of air equal to the volume which the weighed quantity of substance would occupy in the form of a gas, if it were possible to convert it to the gaseous condition at ordinary temperature and pressure.

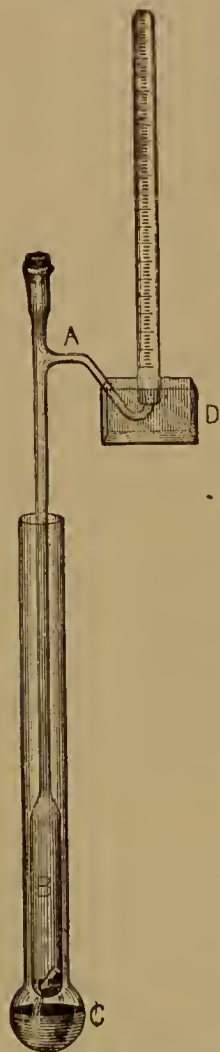


FIG. 16.—VICTOR MEYER VAPOR-DENSITY APPARATUS.

This method leaves nothing to be desired in the way of convenience in execution. Another advantage which it has over others is that the temperature need not be known, to which the apparatus is heated. Indeed, no attention is paid to this in the calculation. It is only necessary that the temperature remain constant during the experiment.

The calculation is as follows:  $g$  mg. of substance were weighed out and found to yield  $V$  c.c. air (measured over water, the water-level outside and inside the tube being the same); the barometer height is  $H$ , the temperature  $t$ , and the tension of water vapor at this temperature  $b$ . The  $g$  mg. of substance, in other words, occupy a volume of  $V$  c.c. at a pressure of  $H-b$  mm. and

$t^\circ$ , so that under these conditions  $\frac{g}{V}$  mg. are contained in the unit volume (1 c.c.)

1 c. c. hydrogen at  $H-b$  mm. pressure and  $t^\circ$  weighs, in milligrams,

$$\frac{0.0899}{1 + 0.00367 t} \frac{H-b}{760},$$

which gives as the vapor density  $D$  ( $H = 1$ )

$$D = \frac{g}{V} \cdot \frac{1 + 0.00367 t}{0.0899} \frac{760}{H-b}.$$



The method of VICTOR MEYER is generally unavailable where the substance in question decomposes on boiling under ordinary pressure. Such substances can often be vaporized at a *lower* pressure without decomposition. In determining their vapor-densities the *method of* HOFMANN can be employed, which was in general use before VICTOR MEYER devised his method, but is now very seldom used, since it is so inconvenient. In the HOFMANN method a weighed quantity of substance, enclosed in a very small bottle with ground stopper, is introduced into the vacuum of a barometer-tube. The latter is surrounded by a glass jacket, through which the vapor of a boiling liquid flows, whose boiling-point is above that of the substance concerned. The weight of substance, the volume of vapor, the height of the mercury, the air-pressure and the temperature furnish the required data.

As to (2): In order to understand how AVOGADRO'S hypothesis can furnish an idea of the number of atoms which the molecules of elements and of compounds contain, let us now return to the example of the synthesis of hydrochloric acid. One vol. hydrogen unites with 1 vol. chlorine to form 2 vols. hydrochloric acid. According to the above law there must be just as many molecules present in the two volumes of hydrochloric acid as molecules of hydrogen and chlorine together. It is evident that this is only possible when the molecules of hydrogen and of chlorine divide into two parts. For, if the chlorine and the hydrogen molecules consisted of only one atom each, the volume of hydrochloric acid could not, in accordance with AVOGADRO'S law, be double that of its elements, but would have to be equal to it. It therefore follows that an even number of atoms must be present in the chlorine and in the hydrogen molecules; whether or not this number is two, as AVOGADRO assumed, can evidently not yet be determined; we shall therefore represent the molecules of hydrogen and of chlorine by  $H_{2x}$  and  $Cl_{2y}$ . From the synthesis of water the same conclusion is reached in regard to the oxygen molecule: 2 vols. hydrogen unite with 1 vol. oxygen to form 2 vols. steam. In each of these two volumes of steam there must be, according to AVOGADRO'S law, just as many molecules present as in the one volume of oxygen. This is likewise impossible unless the oxygen molecule splits into two parts, each of which combines with a molecule of hydrogen, so that we obtain  $H_{2x}O_x$  as the formula of water and  $O_{2z}$  as that of the oxygen molecule.

33. The formulæ for hydrochloric acid, for water and for the molecules of hydrogen, chlorine and oxygen can be fully established,

if the values  $x$ ,  $y$ , and  $z$  are known. These can be ascertained generally in the following way:  $x$  must be at least equal to 1; if this is the case, the molecule of hydrogen becomes  $H_2$ . That a smaller number of atoms is impossible is shown by the synthesis of hydrochloric acid. The vapor densities of a series of hydrogen compounds, as compared with that of hydrogen, are then determined, from which we can find their molecular weights, based on the hydrogen molecule as unity. Thereupon these compounds are analyzed and the amount of hydrogen calculated that is represented in the different molecular weights. It will then be found that in no case is the amount less than half of that in a molecule of hydrogen. Since therefore no compound contains less than half a molecule of hydrogen, the atomic weight of hydrogen must be half its molecular weight, i.e. the formula of the hydrogen molecule is  $H_2$ . Similarly it is found that the oxygen molecule is  $O_2$ , that of chlorine  $Cl_2$ ; in other words, that  $x$ ,  $y$ , and  $z$  are all equal to 1.

*Examples:* (a) 1 l. hydrochloric acid weighs 18.25, when the weight of 1 l. hydrogen is 1. Now in 18.25 parts, by weight, of hydrochloric acid there are 0.5 parts of hydrogen, since 2 vols. (altogether 36.5 parts, by weight) hydrochloric acid are formed from 1 vol. (1 part) hydrogen and 1 vol. (35.5 parts) chlorine. In the hydrochloric-acid gas there is therefore half as much hydrogen per unit volume (molecule) as in a molecule of the latter.

(b) 1 l. steam weighs 9, when the weight of 1 l. hydrogen is 1. According to analysis and synthesis, 9 parts, by weight, of water consists of 1 part of hydrogen and 8 parts of oxygen. The amount of hydrogen contained in one molecule of water is therefore equal to that in a molecule of hydrogen. The amount of oxygen per unit volume (molecule) in water is, however, only half a molecule, for 1 l. oxygen weighs 16 when the same volume of hydrogen weighs 1.

#### RULES FOR DETERMINING MOLECULAR AND ATOMIC WEIGHTS.

**34.** When the atomic weight of hydrogen is taken as unity, its molecular weight is 2. If the specific gravity of another gas based on hydrogen is  $a$ , its molecules weigh  $a$  times as much as those of hydrogen, so that the molecular weight of this gas becomes  $2a$ . The

following rule has therefore been prescribed for the determination of the molecular weight. *Determine the vapor density of the compound, based on hydrogen, and multiply the result by 2; the product is the molecular weight.*

For determining the atomic weight the following holds good, according to § 33: *Determine the composition of molecular amounts of as many compounds of the element as possible; the smallest amount of the element that is found is the atomic weight.*

35. AVOGADRO'S hypothesis has been confirmed from a physical standpoint. It is at present one of the principal laws of chemistry and physics. Let us briefly examine, among others, the physical arguments in its favor. The molecules of bodies, solids as well as liquids and gases, are in constant motion, the intensity of which increases and decreases with the temperature. In different substances at the same temperature there must be a definite relation between the intensities of the molecular movements. This relation has been successfully worked out from the theory in the case of gaseous substances (§ 22, 3). It has been shown that in all gases at the same temperature the mean kinetic energy of translation of a molecule is the same.

The pressure which a gas exerts against the walls of the vessel is caused by the impact of the molecules. We will call the number of molecules in a volume of the gas  $n$ , their mass  $m$  and their mean velocity  $u$ . It is then clear that the gas pressure—the above explanation of its cause being accepted—must be proportional to  $n$  and  $m$ . Moreover the pressure must also be proportional to  $u^2$ , for if the velocity were increased the enclosing walls would receive more impacts from the molecules moving to and fro, and every impact would also become stronger. The gas pressure is therefore proportional to the product  $nm u^2$ ; the theory says that  $p = \frac{1}{3}nm u^2$ , or  $n = \frac{3p}{m u^2}$ .

In this expression  $m u^2$  is twice the kinetic energy of translation of molecules, which is the same for all gases at the same temperature. If then  $p$  is made the same for the different gases,  $\frac{3p}{m u^2}$ , or  $n$ , the number of molecules per unit volume, must be the same for all gases.

## OZONE.

36. As early as 1785 VAN MARUM observed that when an electric spark passes through oxygen a peculiar, "garlic-like" odor is given off, and a bright mercury surface is at once made dull. SCHÖNBEIN investigated this phenomenon more carefully, and found that it is due to the formation of a peculiar substance, which he called

*ozone*. This proved to be oxygen existing in a peculiar condition. The fact, demonstrated by MARIGNAC, that it really consists of nothing but oxygen is shown by its formation from perfectly dry oxygen under the influence of electric discharges, e.g. induction sparks. The amount of ozone thus formed is nevertheless small. It is greater when silent discharges are used. This is one of the best ways of obtaining ozone; at best, however, it yields only 5.6%. Fig. 17 represents the apparatus constructed for this purpose by BERTHELOT.

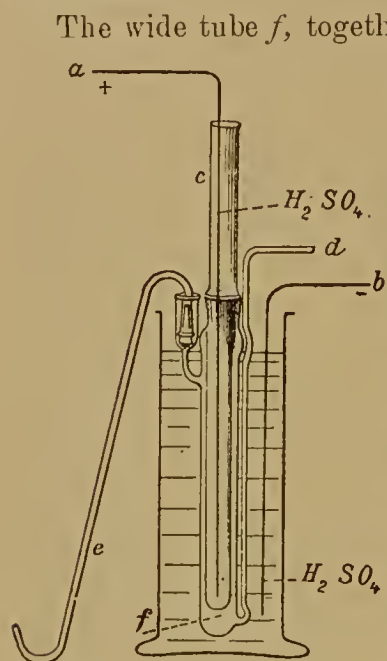


FIG. 17.—PREPARATION OF OZONE.

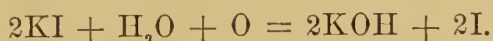
The wide tube *f*, together with the supply tube *d* and the exit tube *e*, are sunk in a vessel of sulphuric acid, into which the pole of the inductor is dipped. The other wire *a* of the latter ends in a tube *c*, which is slipped down inside *f* and is almost entirely filled. The silent discharge between the two bodies of sulphuric acid thus passes through a thin layer of oxygen and has a powerful ozonizing effect.

Ozone is formed in many reactions, such as the slow oxidation of moist phosphorus; also in a small quantity, when hydrogen burns in an atmosphere of oxygen. The oxygen that is obtained by the electrolysis of dilute sulphuric acid always contains it. Ozone is also given off by the decomposition of permanganic acid that is set free in the reaction of potassium permanganate and concentrated sulphuric acid (*cf.* also § 52).

*Physical Properties.*—At ordinary temperatures ozone is a gas of a peculiar odor, having a bluish color in thick layers. By compressing it (slowly, to avoid warming) at a low temperature, or by cooling it through the evaporation of liquid oxygen, it can be condensed to an indigo-blue liquid, which can be separated fairly well from the more volatile oxygen by fractional distillation. Ozone boils under normal pressure at  $-119^{\circ}$ .

*Chemical Properties.*—Ozone is characterized above all by its

ability to oxidize vigorously at ordinary temperatures, especially in the presence of moisture. Phosphorus, sulphur, and arsenic are oxidized to phosphoric acid, sulphuric acid, and arsenic acid, respectively, ammonia to nitric acid, and silver and lead to peroxides; iodine is deposited from a solution of potassium iodide:



Organic substances are strongly oxidized by ozone, hence no apparatus containing it should have connections of rubber. Dye-stuff solutions, like indigo and litmus, are decolorized (by oxidation). Ozone effectively destroys micro-organisms, and is therefore used successfully in the sterilization of drinking-water.

Some of these oxidation phenomena can be used for the detection of ozone, particularly those in which colored compounds are formed. A strip of paper saturated with a weak solution of starch and potassium iodide turns blue in ozone, the iodine combining with starch to form a blue substance. There are, however, many other substances (chlorine, bromine, oxides of nitrogen), which liberate iodine from potassium iodide; hence the following is a safer test for ozone: A strip of violet litmus paper, after being dipped in the iodide solution, is held in the gas to be tested for ozone; if ozone is present, there is formed, besides iodine (compare the above equation) potassium hydrate, which turns the litmus paper blue. Strips of paper upon which thallos hydrate has been placed turn brown in ozone; black lead sulphide is oxidized to white lead sulphate, etc. The action of ozone on mercury is very characteristic; slight traces deprive the metal of its mobility and its lustre and cause it to adhere to glass, forming a reflective surface. An alkaline solution of *m*-phenylene diamine becomes bordeaux red in ozone; neither hydrogen peroxide nor nitrous acid, both of which give many other reactions similar to ozone, show this color test; it is therefore useful in identifying ozone in the presence of these two compounds.

Ozone is stable at ordinary temperatures, but is easily changed to oxygen on heating. It is slightly soluble in water.

#### FORMULA OF OZONE.

37. The determination of the formula of ozone was attended with great difficulties, because it is hardly possible to obtain the substance in a pure state; only mixtures of oxygen and ozone could be investigated. It has, however, been possible to prove that the molecule of ozone contains three atoms of oxygen, while that of

ordinary oxygen possesses only two. This is based upon the following facts:

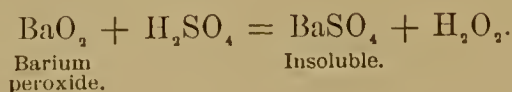
When oxygen is partially converted to ozone, its volume decreases; on heating this ozonized oxygen, it regains its original volume. This decrease of volume unquestionably shows that the ozone molecules do not consist of single oxygen atoms, since—according to AVOGADRO'S law—the volume would then have to increase when ozone is formed. The volume of ozone produced can be determined by dissolving it in turpentine or oil of cinnamon. Let this volume of ozone per 1 l. ozonized oxygen be  $a$  cm.<sup>3</sup>. If another portion of this ozonized oxygen is now heated, in order to reconvert all the ozone into ordinary oxygen, it is found that the increase of volume per 1 l. is  $\frac{1}{2} a$  cm.<sup>3</sup>. It follows from this that  $a$  vols. ozone give  $1\frac{1}{2} a$  vols. ordinary oxygen, i.e. that the specific gravity of ozone must be 1.5 times as great as that of oxygen. If this is the case, the ozone molecule must weigh one-half as much again as that of oxygen. If the latter is O<sub>2</sub>, the former must be O<sub>3</sub>.

In an oxidation by ozone the volume of the ozoniferous gas remains unchanged. Only the third atom in O<sub>3</sub> has oxidizing power, not all three atoms of the molecule.

In ozone we have become acquainted with oxygen that is different from the ordinary kind. This phenomenon is also seen in other elements; it is called *allotropism*.

### HYDROGEN PEROXIDE. H<sub>2</sub>O<sub>2</sub>.

38. This compound is usually prepared by treating barium peroxide with dilute sulphuric acid:



Finely powdered barium peroxide is added to the dilute acid and a dilute solution of hydrogen peroxide is obtained. Since barium peroxide always contains traces of iron, manganese, aluminium, and other oxides, that cause decomposition during the subsequent process of concentration, these must be removed,—preferably by addition of a little baryta water, which precipitates them. This is filtered and the excess of baryta in the filtrate is precipitated by the exact amount of dilute acid and removed, after which the aqueous solution is concentrated. To obtain hydrogen peroxide

free from water, it is fractionated *in vacuo*. THENARD, the discoverer of this compound, concentrated the aqueous solution by placing it in a vacuum over sulphuric acid.

Hydrogen peroxide is also formed in many other ways; e.g. together with ozone (§ 36) in the slow oxidation of phosphorus; by the combustion of hydrogen, when the flame is cooled by a piece of ice. The formation of hydrogen peroxide has been often detected when nascent hydrogen comes in contact with oxygen molecules. We suppose that in the moment just after hydrogen is set free, its atoms have not yet united to form molecules, so that the individual atoms possess unusual chemical activity. This is the general conception of the *status nascendi*. Thus TRAUBE has observed the following instances of the production of hydrogen peroxide: Zinc-filings, when shaken with water and oxygen or air, give hydrogen peroxide, since the zinc and the water generate a small quantity of hydrogen, which unites with the oxygen. Palladium hydride behaves likewise when brought in contact with water and air. In this case it is the hydrogen released from the palladium compound that unites with oxygen. Many metals, such as copper, lead and iron, yield hydrogen peroxide on shaking them with air and dilute sulphuric acid, for the same reason as in the case of zinc and water. Finally, the peroxide is formed in the electrolysis of water, when a current of air or, better, oxygen passes over the negative electrode (at which hydrogen is evolved).

The presence of hydrogen peroxide in many oxidations has led to the supposition that it plays a rôle in all oxidizing processes, it being thought that hydrogen peroxide is first formed and that it then gives up its oxygen for oxidation. According to this view oxidation would be impossible where no water or hydrogen compound is present. In reality it has been determined that, if all moisture is excluded, combination with oxygen frequently does not take place. A piece of phosphorus, for example, which ignites in moist air at a rather low temperature, can be heated up to 150° in an atmosphere of oxygen, without taking fire, if the oxygen has been dried by phosphorus pentoxide. Carbon monoxide, CO, burns with much greater difficulty in dry than in moist oxygen (§ 183). On the other hand, the fact that combustion really occurs to some extent even in dry oxygen speaks against the above supposition. To this one may, of course, reply that it is never possible to remove every trace of moisture; one molecule of water would be sufficient to bring about the reaction, and the retardation of reactions, when the oxygen used is most carefully dried, could be attributed to the fact that only extremely minute traces of water are present.

*Physical Properties.*—In the pure anhydrous condition hydrogen peroxide is a colorless, slightly viscid liquid, having a specific gravity of 1.4584 at 0°, based on water at 4°. (A density calculated on this basis is indicated by  $d_4^0$ .)

*Chemical Properties.*—Hydrogen peroxide, when wholly free from impurities, especially from suspended particles of solid matter, is quite stable and can be distilled *in vacuo*; when impure, it decomposes quite rapidly, however, into water and oxygen, as it also does in dilute solution. In the latter state it is more stable in the presence of traces of acid than in the presence of bases. It is an interesting fact that it decomposes rapidly in contact with powdered substances, apparently without acting upon them. Finely divided silver, gold, platinum (platinum black), and especially manganese dioxide decompose it with effervescence (due to escaping oxygen). Even rough surfaces have a disturbing effect; BRÜHL observed, for instance, that a concentrated solution of hydrogen peroxide evolves oxygen when poured upon ground glass. All these actions must be regarded as catalytic accelerations of the ordinarily very slow decomposition of hydrogen peroxide. The effect of heat is here, as elsewhere, to accelerate the reaction, water and oxygen being formed; concentrated preparations are often exploded thereby.

The *oxidizing action* of hydrogen peroxide is an important chemical property. This is always due to the surrender of an oxygen atom, which effects the oxidation, while water remains. Lead sulphide,  $PbS$ , is oxidized by a weak solution of hydrogen peroxide to lead sulphate,  $PbSO_4$ ; sulphuretted hydrogen,  $H_2S$ , is made to deposit sulphur, water being formed. Barium, strontium, and calcium hydroxides,  $Ba(OH)_2$ ,  $Sr(OH)_2$ , and  $Ca(OH)_2$ , are precipitated by dilute hydrogen peroxide from their solutions as peroxides of the general formula  $MO_2, n. aq.$ <sup>1</sup> The colorless solution of titanium dioxide in concentrated sulphuric acid is turned orange-red by hydrogen peroxide—lemon-yellow by traces of it—on account of the formation of yellow trioxide,  $TiO_3$ . This is a delicate *test for hydrogen peroxide*. Other tests are found in the following oxidation reactions: Potassium iodide starch-paste is at once turned blue by hydrogen peroxide in the presence of a little ferrous sulphate,  $FeSO_4$ . Other oxidizing agents are also able to set

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<sup>1</sup> Aq. (*aqua*), a frequently used abbreviation for 1 molecule  $H_2O$ .



iodine free from potassium iodide (§ 36), but not in the presence of ferrous sulphate (which is itself easily oxidized). A very characteristic reaction is this: Chromic acid solution ( $\text{H}_2\text{CrO}_4$ ) when treated with hydrogen peroxide, is changed to a higher oxide (see § 295) which is blue in aqueous solution and may be taken up by ether if shaken with the latter. This test is, however, less delicate than the two preceding.

A third group of chemical effects of hydrogen peroxide depends on its *reducing power*. When silver oxide is introduced into a solution of hydrogen peroxide, a vigorous evolution of oxygen occurs, water and metallic silver being formed at the same time. Potassium permanganate solution loses its color when mixed with a hydrogen peroxide solution acidulated by sulphuric acid, oxygen being given off rapidly.



The brown peroxide of lead,  $\text{PbO}_2$ , is reduced to reddish-yellow lead oxide,  $\text{PbO}$ .

Ozone and hydrogen peroxide yield water and oxygen; when dilute, they are, however, able to exist side by side.

There is a test for hydrogen peroxide, depending on its reducing power, which is even more delicate than those described above. A mixed solution of ferric chloride and red prussiate of potash has a red color. On the addition of hydrogen peroxide prussian blue is precipitated. Traces of the peroxide turn the solution green.

The ability of so powerfully oxidizing a substance as hydrogen peroxide to act also as a reducing agent can be explained as follows: One of its two oxygen atoms must be loosely joined to the molecule, since it is easily given up. All the substances which are reduced by hydrogen peroxide, also have one loosely held oxygen atom; silver oxide, potassium permanganate, ozone and others give up their oxygen at rather low temperatures. It is therefore possible that the mutual attraction of the oxygen atoms, which tends to make them form oxygen molecules, is stronger than the force by which they are held in hydrogen peroxide on the one hand, and the respective oxygen compound on the other.

*Uses of Hydrogen Peroxide.*—The colors of old paintings are often restored by means of it. The darkening of them is due in many cases to

the transformation of white lead,  $\text{PbSO}_4$ , to black lead sulphide. The latter is readily oxidized by hydrogen peroxide back to white lead sulphate. Hydrogen peroxide is also of value in bleaching ivory, silk, feathers, hair, bristles and sponges. It is also important in analysis.

39. The *composition* of hydrogen peroxide was established by THÉNARD as early as 1818. He first concentrated it in a vacuum and then introduced a weighed amount of it (enclosed in vial) into a graduated barometer-tube over mercury. The vial was then broken and its contents decomposed by heating the tube from without or allowing finely powdered manganese dioxide to rise in the tube. It was thus found that very nearly 17 parts of hydrogen peroxide by weight yield 8 parts of oxygen, water being also formed. One atom of oxygen (16 parts by weight) is therefore obtained from 34 parts of hydrogen peroxide, the remaining 18 parts forming water; in other words, hydrogen peroxide is 1 molecule  $\text{H}_2\text{O} + 1$  atom O. The peroxide therefore contains one atom of oxygen to every hydrogen atom. Its simplest formula (the so-called *empirical formula*) is then HO. Whether this also expresses the molecule or whether the latter is a multiple of it, remains to be determined by finding the molecular weight, inasmuch as every compound of the general formula  $(\text{HO})_n$  possesses the same composition, viz., 16 parts by weight of oxygen to 1 part of hydrogen.

On account of the instability of this substance its vapor density can not well be determined. It was therefore necessary, in finding its molecular weight, to follow another course, which is based on the properties of dilute solutions. In this manner the molecule of hydrogen peroxide was found to possess the formula  $\text{H}_2\text{O}_2$ . The method referred to is explained in the following sections.

#### MOLECULAR WEIGHT FROM THE MEASUREMENT OF THE DEPRESSION OF THE FREEZING-POINT AND ELEVATION OF THE BOILING-POINT.

40. Certain membranes possess the peculiar property of allowing a solvent, e.g. water, to pass through, but not the dissolved substances. They bear the name "*semi-permeable membranes*." This property appears to depend not so much on a sort of sieve action as upon the ability of the membrane to dissolve, or else to

absorb or loosely combine with, the solvent on one side and release it again on the other while the dissolved matter remains behind. One of the ways of obtaining a semi-permeable partition is by dipping a porous cup—such as is used in galvanic cells—containing a solution of yellow prussiate of potash into a solution of blue vitriol. A thin layer of copper ferrocyanide is thereby formed in the wall of the cup, making it semi-permeable. If a dilute sugar solution, salt solution or the like be poured into such a cup and the cup placed in a dish of water, it will be found that the dissolved substance does not diffuse through this sort of a partition. The water does go through, however, for if the cup be closed with a perforated stopper through which a glass tube passes and then dipped deep enough under water so that the entire cup is submerged, the water will be seen to rise slowly in the tube till it reaches a definite height.

The pressure exerted by this column of liquid is called the *osmotic pressure* of the solution. If a tight-fitting piston were inserted in the cup, the force which one would have to exert on it to prevent the infiltration of the water would be equal to the pressure of the column of liquid, for the water continues to rise in the tube till the pressure of the column prevents the entrance of any more. According to researches of VAN'T HOFF the osmotic pressure, like the pressure of gases, obeys the laws of BOYLE and GAY LUSSAC.

If the pressure exerted at a certain temperature by  $a$  kg. of a gas in a vessel be  $p$ , the pressure which  $na$  kg. of the gas at the same temperature exerts in the same vessel is  $np$ . The *concentration*, i.e. density, of the gas has been multiplied  $n$ -fold.

If the osmotic pressure of a solution containing  $a$  per cent of a substance be determined and found to be  $p$ , the osmotic pressure will be  $np$ , if an  $na$  per cent solution of the same temperature be taken, i.e. if the concentration be  $n$  times as great.

An investigation of the pressures which a gas of constant volume exerts at the absolute temperatures  $T_1$  and  $T_2$  shows that these pressures bear to each other the ratio  $T_1 : T_2$ . The same proportion is observed when the osmotic pressure of a solution of constant concentration is measured at the same absolute temperatures as above.

41. The proof of the last statement is furnished by thermodynamics. The existence of a definite ratio between the osmotic pressure and the con-

centration of dilute solutions can be demonstrated in the following way: The pressure which a gas exerts on the walls of the containing vessel is due to the impacts of the molecules of the gas against them. Similarly the osmotic pressure can be considered as caused by the impacts of molecules of the dissolved substance upon the semi-permeable partition. The molecules of the solvent which come in contact with the partition can produce no pressure, since they are able to pass through freely. If the concentration is increased  $n$ -fold,  $n$  times as many molecules of the dissolved substance will strike against the partition in the unit of time and the pressure will become  $n$  times as great. From this it follows that the law of BOYLE strictly applies only to dilute solutions. Concentrated solutions, like gases under high pressure, behave differently. The same may be asserted in regard to GAY LUSSAC'S law.

The laws of osmotic pressure find experimental confirmation in measurements which were made by PFEFFER previous to VAN'T HOFF'S enunciation of the laws. PFEFFER investigated dilute sugar solutions and used an apparatus not unlike the one just described.

The gas laws are expressed by the equation

$$PV = RT, \quad . . . . . (1)$$

in which  $P$  represents the pressure,  $V$  the volume, and  $T$  the absolute temperature of a gas, while  $R$  is a constant. The volume,  $V$ , is inversely proportional to the concentration, according to the above definition; therefore  $\frac{1}{C}$  may be substituted for  $V$ , if  $C$  indicates the concentration. The above equation then becomes

$$\frac{P}{C} = RT,$$

or, at a constant temperature,

$$\frac{P}{C} = \text{Const.}$$

This equation must also be applicable to osmotic pressure. This was really the case in PFEFFER'S measurements of aqueous sugar solutions of different concentrations, as may be seen from the following brief table. The temperature varied between 13.5° and 16.1°, and hence was not perfectly constant:

$C$ :	$P$ .	$\frac{P}{C}$ .
1%	535 mm.	535
2%	1016 "	508
4%	2082 "	521
6%	3075 "	513

The differences in the values of  $\frac{P}{C}$  must be ascribed to the variations of temperature and the unusual experimental difficulties which attend such measurements.

From equation (1) it also follows, when  $V$  (or  $C$ ) is a constant, that

$$\frac{P}{T} = \text{Const.}$$

This conclusion, too, was demonstrated experimentally by PFEFFER in the case of sugar solution, as may be seen from the following table. A one per cent solution was used :

$P$ .	$T$ .	$\frac{P}{T}$
510	287.15	1.7761
520.5	288.5	1.8041
544	305	1.7836
567	309	1.8349

VAN'T HOFF has further shown that the numerical value of the osmotic pressure is the same as that of the gas pressure; that is to say, when a definite amount of a substance in the gaseous state occupies a given volume, the gas pressure which it exerts is just as great as the osmotic pressure which would be produced if the same amount of substance were dissolved in a liquid making the same volume of solution.

The measurements of PFEFFER also furnished experimental proof for this. He found that a 1 per cent sugar solution at  $7^\circ$  exerts a pressure of  $\frac{2}{3}$  of an atmosphere. Such a solution contains 1 g. sugar in 100.6 c.c. Since the molecular weight of sugar is 342, one gram is the 342d part of a gram-molecule. If, then, there is really an equality between the osmotic and the gas pressures,  $\frac{1}{342}$  gram-molecule of any given gas occupying 100.6 c.c. at  $7^\circ$  must exert a pressure of  $\frac{2}{3}$  of an atmosphere;  $\frac{1}{342}$  gram-molecule of a gas whose molecular weight is  $a$  therefore weighs  $\frac{a}{342}$  g. If now we calculate the weight of 100.6 c.c. of this gas at  $7^\circ$  and 1 atm. pressure, we find it to be  $\frac{1}{2}a \times 0.00879$  g., since 0.00879 g. is the weight of 100.6 c.c. hydrogen at the above temperature and pressure.

The pressure which  $\frac{a}{342}$  g., filling this volume, exerts is therefore found by dividing  $\frac{a}{342}$  by  $\frac{1}{2}a \times 0.00879$ , thus :

$$\frac{a}{342} \frac{1}{\frac{1}{2}a \times 0.00879} = \frac{2}{3} \text{ atmosphere,}$$

from which the equality of gas pressure and osmotic pressure is evident.

42. It follows from the preceding that AVOGADRO'S law must also hold for dilute solutions. Assuming that an equal number of molecules of different substances are dissolved in equal volumes at the same temperature, we know from the equality of gas pressure and osmotic pressure that the various substances will exert the same osmotic pressure; inversely, in equal volumes of solution having the same temperature and osmotic pressure there is the same number of molecules.

This is a very important extension of AVOGADRO'S law. It not only becomes possible to compare with each other the weights of equal gas volumes at the same temperature, and deduce therefrom the molecular weight, but we also know that in solutions of the same temperature and the same osmotic pressure the quantities of the dissolved substances contained in equal volumes of solution are to each other as their molecular weights.

Just as it is possible to ascertain the molecular weights of gaseous bodies from determinations of temperature, pressure, weight and volume, it is also possible to find those of substances in dilute solution by measuring the volume of liquid, the temperature, the quantity dissolved and the *osmotic* pressure. The molecular weights of all substances that dissolve in some liquid or other can be determined in this way, and, since the number of soluble substances is very large, there are not a few whose molecular weights were first determined in this way.

In working out this method, however, there is a practical difficulty. The osmotic pressure is very hard to determine directly. This would render the whole method of little value, if it were not for the fact that the calculation only requires that it be known whether two solutions have the *same* osmotic pressure, not the absolute amount of the latter; the law of AVOGADRO simply requires the equality of volume, of temperature and of pressure (osmotic or gas), without regard for the absolute value of these factors (between certain limits). Now, it is easy to measure magnitudes which are proportional to the osmotic pressure, and from which it may be seen whether equality of osmotic pressure exists or not. These magnitudes are the **depression of the freezing-point** and the **elevation of the boiling-point**. An explanation of these terms is perhaps necessary:—When a substance is dissolved in a liquid the maximum tension of the vapor is less above the solution

than above the pure solvent at the same temperature, for the particles of the dissolved body attract the molecules of the solvent, hindering the formation of vapor on the one hand, and, on the other hand, facilitating the return of vapor molecules into the liquid. This lowering of the vapor pressure necessarily causes a depression of the freezing-point and an elevation of the boiling-point, as may be proved by the following diagrams. In Fig. 18,  $abc$  represents the vapor-pressure curve of a solvent in the neighborhood of its freezing-point  $b$ ; the part  $ab$  gives the pressures for the frozen matter; the part  $bc$  for the liquid solvent. This latter part is

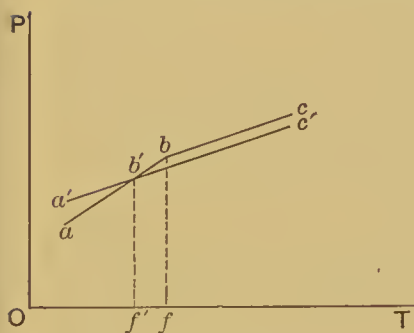


FIG. 18.

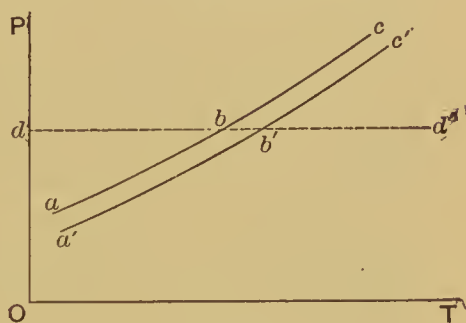


FIG. 19.

always more nearly horizontal than the former, as has been proved both experimentally and theoretically. The freezing-point of a liquid is that temperature at which the solid and liquid states can exist side by side indefinitely. This condition requires that the solid and the liquid substance have the same vapor tension. If, for instance, the vapor tension of the solid were greater than that of the liquid, we should have, at a constant temperature, the vapor given off from the solid condensing to a liquid and the former gradually transformed into the latter. Inversely, if the vapor tension of the solid were less than that of the liquid, the entire liquid would, under similar conditions, solidify.

The freezing-point  $b$  can thus be regarded as the intersection of the vapor-pressure curves  $ab$  and  $bc$  of the solid and the liquid respectively. Let us now consider the curve  $b'c'$  of a solution. Its vapor pressure is lower than that of the pure solvent, so its intersection with the curve  $ab$  must lie more to the left, that is, its freezing-point is lowered. On the other hand, the boiling-point of a solution is that temperature at which the tension of its vapor

equals one atmosphere. If  $Od$  in Fig. 19 represents this tension, a line  $dd'$  parallel to the axis of abscissas will intersect the vapor-pressure curve  $ac$  of the pure solvent at a lower temperature than it will the curve  $a'c'$  of the solution. The latter must, therefore, have a higher boiling-point.

The differences in the freezing- and boiling-points of a liquid before and after the dissolving of a substance are indicated by the above terms.

43. The connection between these magnitudes and the osmotic pressure will be better understood after the following considerations:

1. *Solutions in the same solvent, separated by a semi-permeable partition, can only be in equilibrium when they are isotonic, i. e. when they exert the same osmotic pressure.*

Let us imagine the solutions in an apparatus consisting of two cylinders that are connected by a tube containing a semi-permeable partition. In both cylinders the level of liquid is kept at the same height constantly by adding or removing some from time to time.

The solution with the greater osmotic pressure will extract solvent from the other, for, because of the stronger pressure which the dissolved molecules exert upon the free surface of the liquid, the first solution will endeavor to increase in volume at the expense of the second. Equilibrium will be established so soon as the same pressure is exerted by the dissolved molecules upon the unit area of the free surfaces of the liquids from both sides of the semi-permeable partition; in other words, when the solutions are isotonic.

2. *Isotonic solutions with the same solvent have the same vapor tension at the same temperature.*

The proof of this statement lies in the contradiction to which the

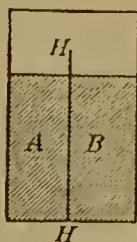


FIG. 20.

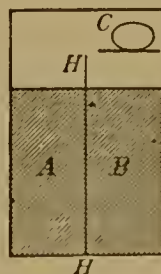


FIG. 21.

assumption that isotonic solutions have unequal vapor tensions leads. The accompanying diagram, Fig. 20, represents a closed vessel, that is separated by the semi-permeable partition  $HH$  into two parts, which contain the isotonic solutions  $A$  and  $B$ . Near the top the two parts are connected with each other. Assuming that the vapor tension of  $A$  is greater



than that of *B*, vapor must pass out of *A* and condense in *B*; the result is that *A* becomes more concentrated, *B* more dilute, and they are no longer isotonic. In such a case, according to the first principle, the solvent would then begin to pass through *HH* from *B* to *A*. The assumption of perpetual motion which is thus made necessary can only be avoided by supposing that the vapor tension is the same.

3. *Isotonic solutions with the same solvent have the same freezing-point.*

Let us again take the same apparatus, containing, in addition to the isotonic solutions *A* and *B*, a piece, *C*, of the solvent in the solid state (Fig. 21). Assuming that *A* and *C* have the same vapor tension, we should have, according to definition (see § 42), the temperature of the freezing-point of *A*. However, if *A* and *B* are isotonic they have the same vapor tension; *B* will, therefore, have the same vapor tension as *C*. Hence *B* and *C* must also be at the temperatures of their freezing-point. At their freezing-points *A* and *B*, therefore, have the same temperature as *C*, i.e. they possess the same freezing-point.

4. *Isotonic solutions with the same solvent have the same boiling-point.*

As we saw in § 42, the boiling-point of a solution is that temperature at which the tension of its vapor equals one atmosphere. Two solutions with a common solvent, therefore, have the same vapor tension at their boiling-point. Now, it was shown above that solutions having the same temperature and vapor tension are isotonic. If these solutions have the same vapor tension (at their boiling-point) and are isotonic, they must also have the same temperature.

Since, as has just been demonstrated, isotonism requires like freezing-points and boiling-points, it is evident the depression of the freezing-point and elevation of the boiling-point must be the same in isotonic solutions with the same solvent.

In the depression of the freezing-point and the elevation of the boiling-point we thus have a means of deciding whether solutions are isotonic. This fact is made use of in the determination of the molecular weight in the following way: The freezing-point of a liquid, e.g. water, pure carbolic acid, etc., is first determined. Thereupon one gram-molecule (*cf.* § 24) of a substance whose molecular weight is known is dissolved in a definite weight (hence also in a known volume) of the liquid. The freezing-point thereby undergoes a definite depression.

This depression of the freezing-point will always be the same, no matter what substance is used, provided a gram-molecule is dissolved in the same volume of the solvent, for such solutions are isotonic.

The depression caused by one gram-molecule is therefore a constant for the particular solvent under consideration.

If we prepare a 1% solution in carboic acid of a substance whose molecular weight,  $M$ , is unknown, and measure the resulting depression,  $\Delta$ , of the freezing-point, we have thus

$$\Delta M = \text{Const.}$$

This formula is evidently applicable to the elevation of the boiling-point also.  $M$  is the only unknown quantity in the equation, and can therefore be easily calculated.

*Example.* When water is used as the solvent, the product of the depression of the freezing-point of a 1% solution and the molecular weight has been found from numerous observations to be 19. We have therefore for water

$$\Delta M = 19.$$

For hydrogen peroxide, the depression of the freezing-point of a 3.3% aqueous solution amounted to  $2.03^\circ$ . This would correspond to  $\frac{2.03}{3.3} = 0.615^\circ$  for a 1% solution; hence  $\Delta = 0.615$ , from which it follows that the molecular weight is  $\frac{19}{0.615} = 30.9$ .

Since the formula HO corresponds to a molecular weight of 17,  $\text{H}_2\text{O}_2$  to one of 34, and the latter number is the nearer to the molecular weight found by experiment, it follows that hydrogen peroxide must be represented by the doubled empirical formula,  $\text{H}_2\text{O}_2$ .

The constant for the depression of the freezing-point (**molecular depression**) has different values for different solvents; for *water* it is 19; for *benzene*, 53; for *nitrobenzene*, 70; for *carboic acid*, 75; for *stearic acid*, 45, etc.

The constant for the elevation of the boiling-point (**molecular elevation**) is 5.2 for *water*, 21 for *ether*, 11.5 for *ethyl alcohol*, 26.7 for *benzene*, etc. These numbers are lower than those for the molecular depression. The value of the molecular elevation is thus smaller than that of the depression, therefore the latter can be determined with greater exactness.

The molecular depression and elevation can be calculated according to the formula  $\frac{0.02T^2}{W}$  (VAN'T HOFF), in which  $T$  represents the absolute temperature of the melting-point or boiling-point and  $W$  the latent heat of fusion or vaporization, respectively.

The determination of the molecular weight by means of the depression of the freezing-point is called the *cryoscopic method*. It can be conveniently carried out with an apparatus constructed by EYKMAN, and called by him a depressimeter (Fig. 22).

The apparatus consists of a short thermometer, divided into twentieths of a degree and fitted at its lower end into the neck of a small flask. The whole is fastened inside of a glass cylinder by means of a stopper at the top and cotton or glass-wool at the bottom. The latter also serves to make the cooling more gradual. A weighed amount of the solvent is introduced into the flask, and its congealing-temperature determined. Thereupon weighed amounts of the substance, whose molecular weight is to be determined, are added, and the freezing-point determined after each fresh addition. In this way the depression for different concentrations is obtained, and in each case the value of  $A$  can be calculated. If these values are then represented graphically by means of a coordinate system, in which the abscissas indicate the concentrations and the ordinates the values of  $A$ , it is very easy to extrapolate  $A$  graphically for infinite dilution, since this value of  $A$  is represented by the point where the line cuts the ordinate axis. This value is then substituted for  $A$  in the formula  $AM = \text{Const.}$  The extrapolation is particularly simple, because, according to the observations of EYKMAN, the values of  $A$  almost always fall upon a straight line. A solvent is employed in which the compound in question is easily soluble, and concentrations are selected between 1% and 10%.

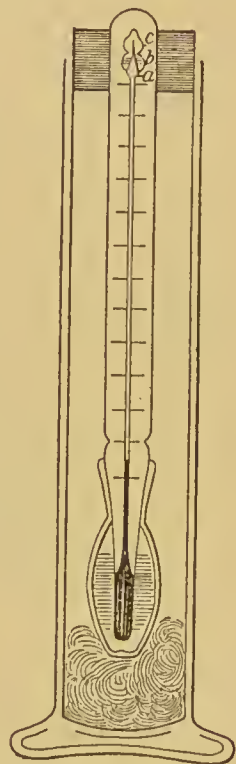


FIG. 23.—DEPRESSIMETER OF EYKMAN.

The apparatus that has been usually employed for the determination of the boiling-point elevation is that suggested by BECKMANN. It consists principally of a glass tube  $A$  (Fig. 23), containing the solution and also some glass beads to make the ebullition more even. This boiling-tube is provided with a reflux condenser  $B$ , inserted into an arm of  $A$ , and also with a thermometer divided into hundredths of a degree, whose bulb dips in the liquid. The

tube *A* is surrounded by a glass vessel *C*, containing some of the same liquid. The latter vessel is heated from below, and in turn

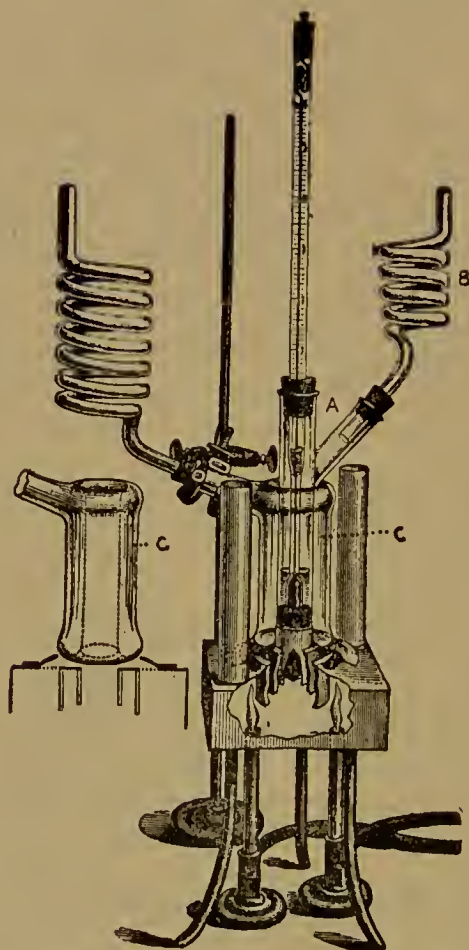


FIG. 23.—BECKMANN'S BOILING-POINT APPARATUS.

warms the real "boiling-tube" within. A constant temperature is all the more necessary in this case, since the molecular elevation is in general smaller than the molecular depression.

A simpler apparatus has been devised by McCoy (Fig. 24). It consists likewise of two vessels, *A* and *B*, fitted tightly together. The inner tube *A* is graduated near the lower end, and is joined to a narrow tube *ab*, opening to the exterior at *a*. A side tube *c* leads from the mouth of *A* to a condenser. The jacket *B* is enlarged at the bottom, and has a side tube *d*, closed by a rubber tube and pinch clamp. About 50 c.c. of the pure solvent and a small piece

of clay tile (to promote regular boiling) are placed in the jacket and 12–16 c.c. of the solvent in the inner tube. The liquid in the jacket is heated to boiling, and its vapor warms the other liquid. As soon as the latter becomes hot, the vapor in the jacket forces its way through *ab* and brings the liquid in the graduated tube to boiling, whereupon a slow distillation into the condenser takes place. Superheating is thus avoided. The reading may be taken within 5–10 minutes from the start. On cooling, *d* is opened to prevent the liquid from being sucked out of the graduated tube. The boiling-point of the pure liquid having been found, a carefully weighed portion of the substance, whose molecular weight is to be determined, is introduced in *A* by lifting the thermometer and cork. After the boiling-point of the solution is determined, the boiling is stopped, the thermometer removed and the volume of the solution taken. The formula is the same as that above, volume being substituted for weight, and the constant calculated on that basis.

### BROMINE.

44. This liquid element does not occur free upon the earth because of its strong tendency to form compounds. In combination with metals it is found in the salts of sea-water. It was discovered in the latter by BALARD in 1826. Bromides occur in rather large amounts in the so-called *Abraum-salze* of the Stassfurt salt-mines.

In the neighborhood of Stassfurt, Germany, there are extensive beds of rock-salt (halite). Above the halite are found layers of other salts (called "*Abraum-salze*" because they have to be removed in order to get at the halite). These salts were formerly rejected as worthless, but they have since been found to be rich in potassium salts, bromides, and other valuable minerals, so that the "waste salts" of former days are now the leading source of many commercially and scientifically important compounds.

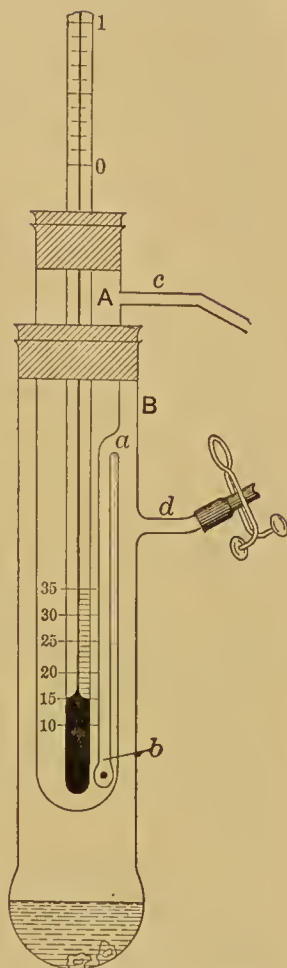


FIG. 24.—McCoy's BOILING-POINT APPARATUS.

The purification of these Stassfurt salts is accomplished by solution in water and partial evaporation of the latter. Various substances crystallize out, while the remaining liquid ("mother liquor") still contains the most soluble salts, among which is magnesium bromide,  $MgBr_2$ . From this mother liquor the bromine is obtained by the use of chlorine, which sets bromine free from bromides, thus:



For this purpose the mother liquor is allowed to flow down through a tower filled with round stones, so that the exposed surface of the liquid is greatly enlarged. A current of chlorine is passed into the tower from below, and, as it rises, the gas is in constant touch with the bromide liquor, the most concentrated gas being in contact with liquor which has already yielded the greater part of its bromine, so that practically all the bromine is thus easily obtained. The bromine prepared in this way always contains a little chlorine, from which it is freed by distillation over finely powdered bromide of potassium.

Another method of obtaining the bromine from the mother liquor is by distilling the latter with manganese dioxide and sulphuric acid, corresponding to the method of making chlorine (§ 25).

The bromine thus obtained still contains a little water. It is dried by shaking it with concentrated sulphuric acid and then distilling again.

*Physical Properties.*—Bromine is a liquid at ordinary temperatures; it is the only element, excepting mercury, that displays this property. It solidifies at  $-7.3^\circ$  and boils at  $59^\circ$ . It is dark brown, and is transparent only in thin layers. It is quite volatile at ordinary temperatures, giving off brown fumes of an extremely irritating and disagreeable odor, whence its name ( $\beta\rho\tilde{\omega}\mu\omicron\varsigma = \text{stench}$ ). Sp. g. = 3.1883 at  $0^\circ$ . 100 parts of water dissolve 3.5 parts of bromine. The addition of potassium bromide to the water increases its solubility a little. Its vapor density is 79.96 ( $O = 16$ ).

*The chemical properties* of bromine are completely analogous to those of chlorine, but the action of the former is less energetic. While, for instance, chlorine combines with hydrogen in the daylight at ordinary temperatures, bromine does not. Its affinity for

many elements is, however, very strong. It reacts vigorously with phosphorus; and powdered arsenic and antimony take fire when sprinkled upon bromine. It is an interesting fact that of the two closely related alkali metals, potassium and sodium, the former reacts vigorously with bromine, while the latter does not react with it at all at ordinary temperatures.

The *bromine molecule* consists of two atoms; for, since its vapor density is 79.96 (see above), its molecular weight must be 159.92. Inasmuch as a gram-molecule of no one of the very numerous bromine compounds contains less than 79.96 g. bromine, but often simple multiples of this quantity, its atomic weight is taken to be 79.96, based on O = 16. The molecule, therefore, contains  $\frac{159.92}{79.96} = 2$  atoms.

#### HYDROBROMIC ACID, or HYDROGEN BROMIDE, HBr.

45. This gaseous compound can be obtained by direct synthesis from its elements; for this purpose it is necessary to pass hydrogen, together with bromine vapor, through a red-hot tube containing finely divided platinum. When a current of hydrogen is passed through bromine, so that it becomes charged with bromine vapor, and it is then ignited, dense clouds of hydrobromic acid arise.

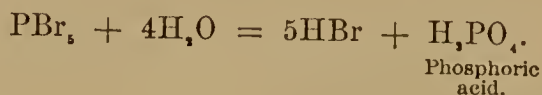
Hydrobromic acid can also be obtained by the action of hydrogen on *bromine compounds*. Silver bromide, AgBr, for example, is reduced by hydrogen at a high temperature to metallic silver with the formation of hydrogen bromide.

On the other hand, it is also formed by the action of bromine on *hydrogen compounds*. For this purpose numerous organic compounds can be used. Sometimes use is made of the action of bromine on naphthalene, C<sub>10</sub>H<sub>8</sub>, the hydrogen bromide, although somewhat impure from the presence of organic substances, being obtained at the ordinary temperature. It is also produced when hydrogen sulphide is led into bromine covered with water, sulphur being deposited at the same time:



The ordinary method of preparing hydrobromic acid depends,

however, on the decomposition of a bromine compound by a hydrogen compound, phosphorus pentabromide,  $\text{PBr}_5$ , and water being employed;



As phosphoric acid is not volatile, but the desired substance is, the two products of the reaction can be easily separated.

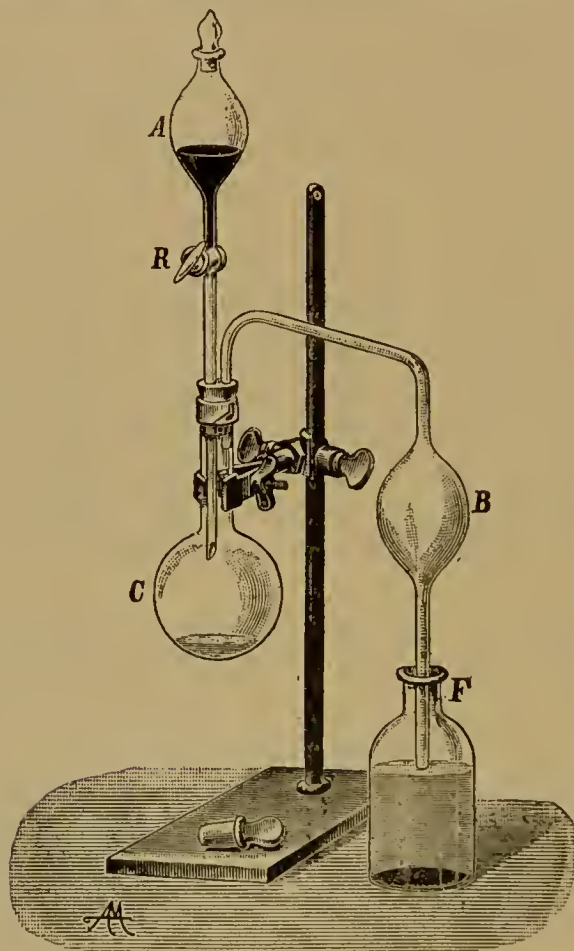


FIG. 25.—PREPARATION OF HYDROBROMIC ACID.

For the preparation of hydrobromic acid by this reaction it is unnecessary to prepare the pentabromide first. If bromine is allowed to fall carefully, drop by drop, upon some red phosphorus under water a steady evolution of hydrobromic acid is obtained.

Fig. 25 shows how this may be done. Bromine is placed in the dropping-funnel *A*, from which it may be allowed to flow down into the flask *C* con-



taining red phosphorus under water, the rate of flow being regulated by the stopcock *R*. The generated hydrobromic acid passes through the doubly bent tube, which has a bulb-shaped dilatation at *B*, into the bottle *F*, where it is absorbed by water. The bulb *B* serves to prevent a backward flow of the water from *F* into the generator *C*.

Another method of preparing hydrobromic acid is by the action of dilute sulphuric acid on a bromide, e.g.  $\text{KBr}$ . On heating the mixture a dilute solution of hydrobromic acid distills over.

Hydrobromic acid has a decomposing action on concentrated sulphuric acid. The hydrogen of the former reduces the latter to  $\text{SO}_2$ , bromine being set free.

*Physical Properties.*—At ordinary temperatures hydrogen bromide is a gas. It can be condensed, by cooling, to a liquid which boils at  $-64.9^\circ$  (under 738.2 mm. pressure), and, by still farther cooling, to colorless crystals, which melt at  $-88.5^\circ$ . It has a piercing odor and a sour taste. In contact with moist air it forms dense clouds, like hydrochloric acid (§ 29). It is very soluble in water, 1 vol. water dissolving about 600 vols. at  $10^\circ$ ; its solubility is thus even greater than that of hydrochloric acid.

*Chemical Properties.*—Here, too, the acidic nature is strongly displayed. Various metals, such as zinc and magnesium, are acted upon by hydrobromic acid, forming a salt and free hydrogen. The most of its salts are soluble in water; silver bromide, however, is insoluble and lead bromide difficultly soluble.

A very high temperature is required to decompose hydrogen bromide into its elements.

The composition of hydrobromic acid can be determined in the same way as that of hydrochloric acid. Since its vapor density is 40.38, it has a molecular weight of 80.76. The atomic weight of bromine being 79.96 ( $\text{O} = 16$ ), it follows that the formula of hydrobromic acid must be  $\text{HBr}$ . Moreover, the dry gas can be decomposed with sodium amalgam, whereby it is found that half of its volume consists of hydrogen; this confirms the above molecular formula.

## IODINE.

46. This element, a crystalline solid, was discovered by COURTOIS in 1812, but its elementary nature was first recognized in 1815 by GAY LUSSAC. Like chlorine and bromine, it does not occur in

the free state, but is frequently found in nature in combination with some metal. An important source of iodine compounds is the mother-liquor (§ 44) remaining in the purification of Chili saltpetre; another, the ash of sea-weeds, known in Scotland as *kelp* and in Normandy as *varec*, which contains iodides. The extraction of the iodine is accomplished either by passing chlorine into the solution or by distilling with manganese dioxide and sulphuric acid in the same manner as for bromine and chlorine. The commercial iodine is purified by warming it gently with the addition of a little potassium iodide, the iodine subliming in the pure state, free from traces of chlorine and bromine that may have been present. Finally, it is dried in a desiccator over sulphuric acid.

*Physical Properties.*—Iodine forms tabular crystals of a dark gray metallic lustre. Its specific gravity is 4.948 at 17°. It melts at 114.2°, and boils under 760 mm. pressure at 184.35°. Its vapor is characterized by a beautiful dark-blue color, which gave the element its name (*ιώδης* = violet). In water it is only slightly soluble—enough, however, to color the water yellow. It dissolves easily in a solution of potassium iodide, the latter being turned brown. In various other liquids, such as alcohol, ether, carbon bisulphide and chloroform, iodine is also easily soluble. It is a peculiar fact that the alcoholic and the ethereal solutions are brown, while the solutions in carbon bisulphide and chloroform are violet; other solvents, e.g. benzene, give solutions of an intermediate color. The cause of this variety of color among its solutions is not yet satisfactorily explained.

47. The vapor density of iodine is 8.72 (air = 1) at about 600°. As the temperature rises, it grows steadily smaller, however. Thus we have :

Temperature.	Vapor Density.
878°	8.11
1030°	6.83
1250°	5.65
1390°	5.23
1500°	4.5

At 1500° we see it is reduced to almost half of what it is at 600°. As we shall later (§ 49) have occasion to discuss this phenomenon, called *dissociation*, which has also been observed in many other substances, it will here suffice to explain how the vapor densities at such elevated temperatures have been determined by V. MEYER and his pupils.

The apparatus he employed (Fig. 26) consists of a cylinder 200 mm. deep and 36 mm. in diameter, connected with which is a 4-mm. tube 350 mm. long. There is also a capillary tube leading to the bottom of the cylinder. The entire apparatus is constructed of platinum. In determining vapor density at a high temperature the apparatus—properly protected from direct contact with the flame—is placed in a PERROT furnace in such a manner that the tube protrudes enough to attach a piece of rubber tubing, connecting the apparatus with a tube provided with a side arm for the escape of gases. The apparatus does not essentially differ from that described above (§ 32) for the ordinary determination of vapor density according to V. MEYER. When the lower part of the apparatus has reached the temperature of the furnace the vapor density is determined in the usual way, a knowledge of the temperature being, of course, just as unnecessary as in the previous case.

VICTOR MEYER, however, was interested in determining not only the amount of the vapor density, but also the way in which it varies with the temperature. To this end it was, of course, necessary to know the temperature at which each measurement was made. This can be ascertained with the help of the self-same apparatus in the following manner: The volume of air (or nitrogen) contained by the apparatus at the ordinary temperature is measured by displacing the air with carbon dioxide, which is passed through a narrow tube to the bottom of the vessel; the air is collected in a graduated tube over a liquid (caustic potash solution) which completely absorbs carbon dioxide. The same operation is repeated subsequently, when the apparatus is glowing hot, as soon as the vapor-density determination is completed and air has been passed through the apparatus for a few minutes in order to expel the vapor of the substance whose density has been determined. The volume of air then present in the apparatus, together with the volume contained at the ordinary (measurable) temperature and the expansion coefficient of air, furnish all the data required for a calculation of the desired temperature. There is, however, one difficulty: only the lower part of the apparatus possesses the temperature to be measured; the adjoining tube and the other parts of the apparatus, such as the glass side-tube, do not. Hence a correction must be introduced in the calculation, which is found with the help of the *compensator* (Fig. 26). This consists of two platinum tubes of exactly the same dimensions, and, therefore, the same capacity, as the two tubes which protrude from the cylinder. To these last-named tubes the compensator is attached by means of platinum wire. It may be assumed that the air in

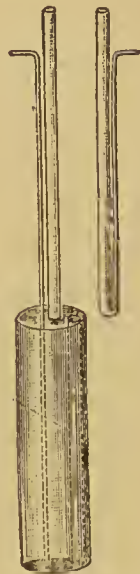


FIG. 26.—APPARATUS FOR THE VAPOR-DENSITY DETERMINATION OF IODINE, AFTER V. MEYER.

the latter has the same temperature as that in the corresponding parts of the real apparatus. It is readily seen that, when the volume of the compensator at the ordinary temperature and that at the temperature at which the determination is made are subtracted from the corresponding volumes of the real apparatus, the remainder is the volume of air contained in the lower wider portion at the temperature of the experiment.

In temperature measurements of this sort the following is also to be noted: The entire method is based on the assumption that the coefficient of expansion of air stays the same at these high temperatures; in other words, that the specific gravity of air remains constant, and does not diminish like that of iodine. This assumption was, however, hardly reliable, and in order to test the matter it would be necessary to measure the volume at a known high temperature, whereas in these experiments the temperature is unknown and must be calculated from the volume. To avoid this difficulty the temperature measurement was carried out with different gases in the same manner as above. The results were the same. Now, it was very improbable that all of the gases employed (oxygen, nitrogen, carbon dioxide, sulphurous oxide and others) should show a decrease of density and all in the same measure. Therefore, it was reasonable to assume that their expansion is normal.

The *chemical properties of iodine* resemble very strongly those of chlorine and bromine. Its affinity for other elements is in general weaker, however, than that of the two halogens mentioned. It combines with metals, e.g. mercury, directly to form salts (iodides). A characteristic test for iodine is the intense blue coloration which it imparts to starch solution; the slightest traces of iodine can be thus detected. The blue color disappears on boiling and reappears on cooling, provided the boiling was not too prolonged.

The *molecule of iodine*, investigated by the same method as was employed with bromine, is found to consist of two atoms at  $600^{\circ}$ , hence the formula is  $I_2$ . Above  $1500^{\circ}$  it must contain only one atom, for the vapor density is less by one-half.

#### HYDRIODIC ACID, or HYDROGEN IODIDE, HI.

48. This compound can be obtained by direct synthesis from its elements, and that is really the best method for preparing it in a perfectly pure state. For this purpose hydrogen and iodine vapor are conducted together over heated platinum-black, which accelerates their combination.

Hydrogen iodide can also be obtained by the reaction of iodine

with hydrogen compounds. Organic hydrogen compounds are preferable, especially colophonium and copaiva oil. This method is also used for the laboratory preparation of the gas, but the hydrogen iodide thus obtained is more or less adulterated with organic substances. When iodine acts on hydrogen sulphide water, hydrogen iodide is formed, sulphur being liberated (§ 45).

As an example of the action of hydrogen on an iodine compound, we may mention the reduction of silver iodide by hydrogen, from which hydrogen iodide results.

Finally, the action of an iodide on a hydrogen compound is illustrated by the decomposition of a phosphorus iodide,  $PI_3$  or  $PI_5$ , by water. As was explained in § 45, it is possible to use phosphorus, iodine and water. This method, with some variation or other, is the preferable one for the preparation of hydriodic acid.

According to GATTERMANN, it is best to first add yellow phosphorus (4 g.) in very small pieces to 44 g. iodine, and then decompose the resulting compound with a little water. In order to remove the free iodine from the hydrogen iodide formed, the gas is allowed to pass over red phosphorus.

The decomposition of the halogen salt by sulphuric acid is even less available for the preparation of hydriodic than hydrobromic acid, since the former is more easily decomposed by sulphuric acid than the latter.

*Physical Properties.*—Hydrogen iodide is a colorless gas, whose specific gravity is 62.94 ( $H = 1$ ). It fumes strongly when exposed to the air, and possesses an acid reaction and a pungent odor. At  $0^\circ$  and 4 atmospheres pressure it condenses to a colorless liquid, which boils under a pressure of 730.4 mm. at  $-34.14^\circ$ . The melting-point of the solid is  $-50.8^\circ$ . Hydrogen iodide is very soluble in water; 1 vol.  $H_2O$  at  $10^\circ$  dissolves 425 vol. HI. This solution fumes strongly, and turns dark brown after a time, because of the liberation of iodine.

*Chemical Properties.*—Hydrogen iodide has all the characteristics of an acid. With metals it forms salts (iodides), hydrogen being given off. These are almost all soluble, with the exception of the iodides of silver and mercury. Lead iodide is slightly soluble at ordinary temperatures. In addition to its acidic character, hydriodic acid possesses another property, which is not found in hydrochloric and hydrobromic acids. Since it splits up readily into hydrogen and iodine, it can act as a strong reducing agent, especially at high temperatures. It has already been remarked that the aqueous

solution of the gas turns brown, iodine being set free by the oxidizing action of the air; this change is greatly aided by the influence of light. At a high temperature hydrogen iodide is decomposed into  $H_2$  and  $I_2$ , as we learn from the appearance of the violet iodine vapor. In organic chemistry, particularly, frequent use is made of the reducing power of this acid.

*Formula of Hydriodic Acid.*—The vapor density of this substance has been found to be 62.94. Its molecular weight is therefore 125.88. The atomic weight of iodine being 125.91 ( $H = 1$ ), it is seen that the molecular weight corresponds very closely to the formula  $HI = 126.91$ , and no other formula is possible.

### DISSOCIATION.

49. When hydrogen iodide is subjected to a slow increase of temperature, it commences to decompose at a definite temperature slightly above  $180^\circ$  into hydrogen and iodine vapor. As the heating continues, the decomposition grows greater without at once becoming complete. After a still further rise of temperature a point is finally reached when only the individual elements exist. If the mixture is then slowly cooled, the same stages are passed through in inverse order, so that the degree of decomposition at any one temperature is found to be the same, no matter whether the temperature was approached from above or below, it being only necessary that the particular temperature should be maintained for a sufficient length of time in both cases.

The phenomenon just described is to be observed with a great many substances. It is called **dissociation**, and was first studied in 1857 by H. SAINTE-CLAIRE DEVILLE.

The degree of decomposition of hydrogen iodide is, as we have seen, always found to be the same for a definite temperature. It necessarily follows from this that if one starts with the uncombined elements, hydrogen and iodine, and heats them together long enough at a certain temperature, a gas mixture of exactly the same composition will be formed as that resulting from the decomposition of the hydrogen iodide at the same temperature. This is confirmed by experiment; e.g. equivalent amounts of iodine and hydrogen were heated in a sealed vessel by exposing it to the vapor of boiling sulphur ( $445^\circ$ ). The amount of hydrogen iodide finally produced

was 78.96%, i.e. 21.04% of the gas mixture remained uncombined. Again, when a like vessel filled with hydrogen iodide was heated to the same temperature, it was found that 21.5% had decomposed—a figure very close to that obtained in the preceding experiment.

Such reactions, which lead to the same result, immaterial whether we start with the one system of substances ( $H_2 + I_2$ ) or with the other ( $2HI$ ), are called **reversible reactions**, or **balanced actions**. When the final stage is reached, the systems are said to be in *equilibrium* with each other.

We saw that in the preparation of hydrogen iodide, platinum-black is used because it accelerates their combination. Neither this nor any other catalyzer, however, changes the ratio in which combination takes place. For instance, it is found empirically that at  $350^\circ$  18.6% of the hydriodic acid is decomposed when no platinum-black is present, and that in the presence of this catalyzer the decomposition reaches 19%; these two figures are alike within the limits of experimental error. There is a theoretical reason why this must be so. If the catalyzer could influence the equilibrium, we should arrive at a perpetuum mobile by successively adding and removing the catalyzer. This would involve a change in the quantity combined, and the energy thus obtained could be used to do work without a sinking of the temperature, which is impossible according to the principles of thermodynamics.

The question now arises, how such an equilibrium comes about, and why the decomposition of a compound that begins at a certain temperature does not complete itself. To this the kinetic theory of gases furnishes a satisfactory answer. According to this theory the molecules of gases are constantly in motion. While a constant *mean* velocity of the molecules may be assumed to exist for every temperature, the velocities of the *individual* molecules must be considerably different, because of the very frequent collisions with each other. The atoms of a molecule must also be supposed to be capable of changing their respective positions, for the repeated collisions of the molecules displaces the atoms from their positions of equilibrium. These movements of the atoms are the more violent the greater the velocity of the molecules. It is easy to conceive that they may at last become so violent as to throw the atoms out of their sphere of mutual attraction. The molecule is thus broken up. In a body of gas at a definite temperature this will, however, only occur in those molecules whose velocity is above certain limits; hence we see a reason for *partial decomposition*. The explanation

of *partial combination* is exactly analogous. The atoms set free from the molecules of the elements enter into the sphere of mutual attraction, and if their velocities are not great enough to resist the attraction, the different atoms unite.

In the case of the formation and decomposition of hydrogen iodide this can be conceived as follows: Two HI molecules meet in such a state of atomic movement that the H atoms enter the spheres of attraction of each other, and the I atoms likewise, so that H<sub>2</sub> and I<sub>2</sub> are formed. On the other hand, these molecules H<sub>2</sub> and I<sub>2</sub> may again meet in such a way that each H atom enters the sphere of attraction of one of the I atoms, whereupon two HI molecules are formed.

According to the above the state of equilibrium is to be accounted for by supposing that in the unit of time just as much passes from the one system into the other, as *vice versa*. Until the state of equilibrium is reached, the amounts which pass from one system into the other in the unit of time are unlike. If we understand by **reaction-velocity** the amount in gram-molecules which is transformed from one system into the other in the unit of time, the **state of equilibrium** may be defined as *that state in which the reaction-velocities of both systems have become equal*.

For the determination of the reaction-velocity a principle of very wide application has been discovered, which allows this magnitude to be calculated mathematically, viz., the principle that *the reaction-velocity at any moment is proportional to the masses of the substances then present*. This is the **law of chemical mass-action**.

50. Let it be assumed that the molecules of a compound are dissociated by heat into two others, the process being expressed by



in which *A*, *B* and *C* represent single molecules. Of the substance *A*, *a* gram-molecules were originally present, but in the course of a definite time, *t*, *x* gram-molecules have undergone the above decomposition. The problem is to express the reaction-velocity at any moment. For this purpose let us consider the very small interval of time,  $\Delta t$ , which immediately follows the period *t*. In the interval  $\Delta t$  a minute amount,  $\Delta x$ , of the substance *A* is decomposed. Then, according to definition, the reaction-velocity, *S*, in that moment is  $\frac{\Delta x}{\Delta t}$ . In accordance with the above-stated principle, this



must be proportional to the amount of  $A$  remaining undecomposed at this moment; that is, to  $a - x$ . The mathematical equation for the reaction-velocity thus becomes

$$S = \frac{\Delta x}{\Delta t} = C(a - x),$$

where  $C$  is a constant factor, the **reaction constant**, or **velocity constant**. This expression does not, however, indicate exactly the reaction-velocity at the close of the period  $t$ , i.e. at the moment when the period  $t$  ends; we are really considering the velocity in the succeeding brief interval  $\Delta t$ . But it is clear that we may approach this value as closely as we please, if we make  $\Delta t$  small enough, so that when  $\Delta t$  becomes infinitesimal, the expression  $\frac{\Delta x}{\Delta t}$  (then written  $\frac{dx}{dt}$ ) may be considered identical with the reaction-velocity in the moment  $t$ .

The above reaction is termed **unimolecular**. When two (like or different) molecules react with each other, the reaction is called **bimolecular**; it may be represented by the equation



The equation for the reaction-velocity is different in this latter case. Assuming that originally  $a$  gram-molecules of  $A$  and  $b$  gram-molecules of  $B$  take part in the reaction, and that  $x$  gram-molecules of  $A$  and of  $B$  are decomposed at the end of the period  $t$ , there must be, respectively,  $a - x$  and  $b - x$  of the two substances present at this moment. The reaction-velocity will then be proportional to the product of these quantities, thus

$$s_1 = \frac{dx}{dt} = C'(a - x)(b - x),$$

in which  $C'$  is again a constant. Since the reaction-velocity must be proportional to the mass of each of the reacting substances, a product is required to express the relation.

It is assumed in the above that the temperature is constant. We shall see in § 104 that this factor has a great influence on the reaction-velocity.

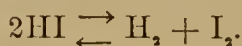
51. The manner of expressing the condition of equilibrium is

now plain. Assuming that the reaction-velocity of the one system is  $S$  and that of the other  $S'$ , equilibrium must exist when  $S = S'$ .

Let us apply these considerations to the dissociation of hydrogen iodide. This may be expressed by the equation



If it is to be indicated that the reaction is reversible, we write



If  $a$  gram-molecules HI per unit volume are present originally and  $x$  of these are decomposed after a given period, the reaction-velocity at this moment (since in this case  $a = b$ , and the reaction is evidently bimolecular) is

$$S = C(a - x)^2,$$

$C$  being a constant.

From the  $x$  gram-molecules of hydrogen iodide  $\frac{x}{2}$  gram-molecules of hydrogen and an equal amount of iodine have been formed. The velocity of formation of HI from  $\text{H}_2$  and  $\text{I}_2$  is therefore expressed by the equation

$$S' = C' \left( \frac{x}{2} \right)^2,$$

in which  $C'$  is a constant. Accordingly equilibrium will exist when

$$C(a - x)^2 = C' \left( \frac{x}{2} \right)^2 \quad \text{or} \quad \left( \frac{x}{a - x} \right)^2 = K,$$

in which  $K$  is substituted for  $\frac{4C'}{C}$ .

This equation may be written in a slightly different way, since in gases the number of molecules per unit volume is proportional to the pressure (§ 31). Assuming that at a given moment the pressure of the hydrogen iodide still present is  $p$ , that of the hydrogen is  $p_1$ , and that of the iodine vapor  $p_2$ , the equilibrium constant,  $K$ , can be represented by the expression

$$\frac{p_1 p_2}{p^2} = K.$$

It has been ascertained that the dissociation is less if the

hydrogen iodide was originally mixed with hydrogen or with iodine vapor. The necessity of this being true follows immediately from the above equation, for the addition of these gases amounts to an increase of  $p_1$  or  $p_2$ . If  $K$  is to remain constant,  $p$ , or in other words the mass of undissociated hydrogen iodide, must increase. We see also from the equation that the same increase of  $\text{H}_2$  or of  $\text{I}_2$  must have the same influence on the equilibrium. A farther conclusion from this equation is that, when  $p$ ,  $p_1$  and  $p_2$  are increased  $n$ -fold, i.e. when hydrogen iodide undergoing dissociation is compressed or expanded at a constant temperature, the degree of dissociation must remain unaltered, since

$$\frac{np_1 \cdot np_2}{(np)^2} = \frac{p_1 p_2}{p^2}.$$

This, too, is confirmed by experiment.

In the dissociation of hydrogen iodide the gas volume does not change, since two molecules ( $2\text{HI}$ ) yield two molecules ( $\text{H}_2$  and  $\text{I}_2$ ). In all such cases the degree of dissociation must be independent of the volume, because an increase or decrease in the latter causes changes in the concentration of the reacting gases which are proportional to each other, and hence the factor representing the concentration falls out of the equation.

Hydrogen iodide is also decomposed by light. It is a peculiar fact that this dissociation is unimolecular ( $\text{HI} = \text{H} + \text{I}$ ), while that caused by rise of temperature is bimolecular. This may be demonstrated by the following very general method. When the reaction is unimolecular, the equation for the velocity of decomposition is  $\frac{dx}{dt} = K(a - x)$ . When, however, it is bimolecular ( $2\text{HI} = \text{H}_2 + \text{I}_2$ ), the equation becomes  $\frac{dx}{dt} = K(a - x)^2$ . With the help of integral calculus these equations can be solved for  $K$ ; from the first we find

$$K = \frac{1}{t} \ln \frac{a}{a - x}, \quad \dots \dots \dots (1)$$

where  $\ln$  is the natural logarithm, and from the second :

$$K = \frac{1}{t} \frac{x}{a(a - x)}, \quad \dots \dots \dots (2)$$

If now we determine  $x$  for various values of  $t$ , the values of  $K$  can be

calculated; they must be constant. If this constancy appears in (1), the reaction is unimolecular, if in (2), bimolecular.

### FLUORINE.

52. This element was first isolated from its compounds by MOISSAN in 1886. It occurs in nature chiefly in combination with calcium as *fluor spar*,  $\text{CaF}_2$ , and in certain rare minerals.

The great difficulty in obtaining it in the free state is due to its very great affinity, which makes it unite with all other elements even at ordinary temperatures. As yet it has only been successfully prepared by the electrolysis of pure anhydrous hydrofluoric acid in which potassium fluoride has been dissolved to make the liquid a conductor.

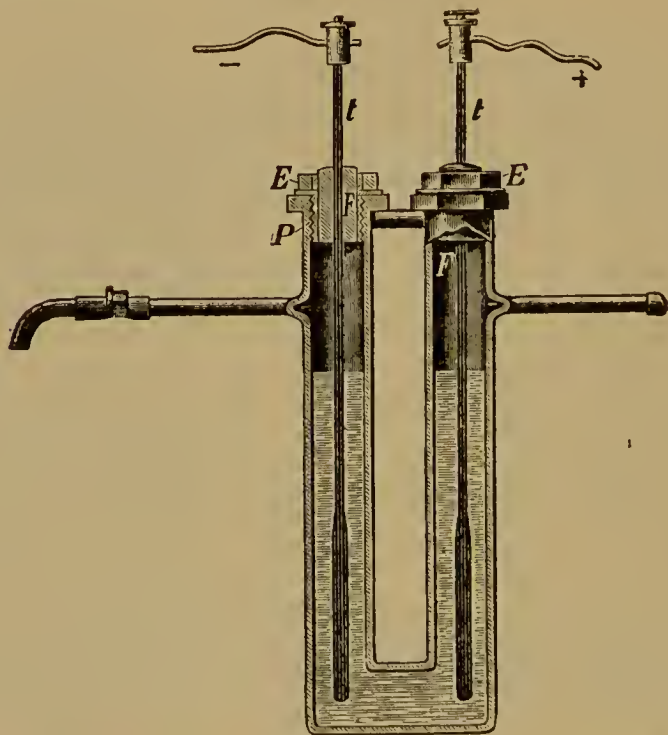


FIG. 27.—PREPARATION OF FLUORINE BY ELECTROLYSIS. (AFTER MOISSAN.)

The manner in which MOISSAN accomplished this is interesting. A mixture of about 200 g. anhydrous hydrofluoric acid and 60 g. potassium fluoride—hydrofluoric acid is introduced into a copper U-tube (Fig. 27) of a capacity of about 300 c.c., which has two lateral exit tubes. The open ends of the U-tube are closed with stoppers *FF*, made of fluor spar and wrapped in very thin sheet platinum.

The cylindrical electrodes *tt* of platinum-iridium pass through the stoppers and are held in place by the copper screws *EE*, which fit tightly to the ends of the U-tube, with the help of a band of lead *P*.

During the electrolysis the apparatus is kept at the constant temperature of  $-23^{\circ}$  (by boiling methyl chloride). The free fluorine, which is given off as a gas at the positive electrode, is first passed through a platinum vessel that is cooled by a mixture of solid carbon dioxide and alcohol, in order to condense the acid fumes which were carried over with it. The last traces of the acid are removed by conducting the gas through two platinum tubes containing sodium fluoride, which absorbs the hydrofluoric acid. The free fluorine gas was collected by MOISSAN in a platinum tube, whose two ends were closed with plates of fluor spar so that one could look through.

Later MOISSAN found that perfectly pure fluorine attacks glass but very slowly, so that the gas may be collected in glass vessels.

*Physical Properties.*—Fluorine is a gas with a very pungent odor and a greenish-yellow color, which is somewhat paler than that of chlorine. As a liquid it boils at  $-187^{\circ}$  and is bright yellow. It can be condensed in a glass vessel. The specific gravity of the gas is 19 ( $O = 16$ ), that of the liquid 1.14 (water = 1).

*Chemical Properties.*—Of all the elements now known fluorine has the strongest tendency to form compounds. It combines with hydrogen in the dark at ordinary temperatures in an explosive manner. MOISSAN demonstrated this with the help of the above apparatus by reversing the electric current while fluorine was being generated; thus a mixture of hydrogen and fluorine was formed, which at once exploded. As low as  $-210^{\circ}$  fluorine unites with hydrogen immediately, producing a flame. Finely divided carbon ignites instantly in fluorine gas, forming  $CF_4$ , while chlorine does not combine with carbon directly even at a high temperature. Fluorine combines with most metals instantly and violently; it does not unite with oxygen, even when it is heated with the latter to  $500^{\circ}$  or mixed in the liquid state with liquid oxygen at  $-190^{\circ}$ . The alkali metals (potassium and sodium) and the alkaline-earth metals (calcium, strontium, barium) take fire in fluorine gas at ordinary temperatures with the formation of fluorides. Finely divided iron glows faintly in it. Copper becomes covered with a layer of copper fluoride,  $CuF_2$ , which protects it against farther corrosion; hence the possibility of employing this metal for fluorine generators. Gold and plati-

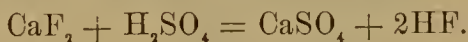
num are not attacked by fluorine,—a rather striking fact, since these metals are acted on by chlorine, which otherwise displays a weaker chemical affinity.

Fluorine reacts readily with hydrogen compounds; e.g. water is decomposed by it at ordinary temperatures into hydrofluoric acid and strongly ozonized (as high as 14% by volume) oxygen. It sets chlorine free from potassium chloride, forming potassium fluoride.

The *molecule* of gaseous fluorine is expressed by the formula  $F_2$ . Its vapor-density being 19, the molecular weight is 38. Inasmuch as no fluorine compound contains less than 19 g. fluorine per gram-molecule, but frequently a multiple of this amount, the atomic weight of fluorine becomes 19 and its molecular formula  $F_2$ .

#### HYDROFLUORIC ACID, OR HYDROGEN FLUORIDE, HF.

53. This compound was discovered by SCHEELÉ in 1771 upon heating together fluor spar and sulphuric acid:



This is still the usual method of preparing the substance. A mixture of powdered fluor spar and dilute sulphuric acid is distilled in an apparatus of platinum or lead, since glass is instantly attacked by hydrofluoric acid. The distillate is an aqueous solution of the acid, which for the above reason must be preserved in bottles of lead or earthenware.

By direct synthesis from its elements (§ 52) hydrofluoric acid may also be obtained. Another method is by the action of hydrogen on a fluorine compound; e.g. silver fluoride, when heated in a current of hydrogen, gives hydrogen fluoride.

Still other methods are by the action of fluorine on hydrogen compounds (§ 52) and by the direct decomposition of certain compounds, such as hydrogen potassium fluoride,  $KF \cdot HF$ , which splits up on heating into the two fluorides. This last reaction is made use of when anhydrous acid is sought.

*Physical Properties.*—Anhydrous hydrofluoric acid is a colorless liquid at ordinary temperatures. It boils at  $19.5^\circ$  and solidifies at  $-92^\circ$ . Sp. g. ( $H = 1$ ) = 0.9879 at  $15^\circ$ . It has an extremely pungent odor and is very poisonous when inhaled. It is very soluble in water.

*Chemical Properties.*—The aqueous solution of hydrogen fluoride, the “hydrofluoric acid” of commerce, possesses entirely the character of an acid; it evolves hydrogen with metals, the precious metals, however, and also lead, being unaffected by it. The fluorides of most metals dissolve in water; some, however, such as those of copper and lead, with difficulty, while those of the alkaline earths (Ca, Sr and Ba) are insoluble. It is a peculiar characteristic of the alkaline fluorides that they are able to combine with a molecule of the acid, forming double fluorides like that described above,  $\text{KF} \cdot \text{HF}$ .

The most important property of the gas for practical purposes is that it attacks glass (*cf.* § 193). As a result it finds extensive use in etching glass.

Glass may be etched in two ways—with a solution of the gas or with the gas itself. In the first case the etching is shiny and transparent; in the second dull. The glass object is covered with a coat of wax in which the figures or letters which one desires etched on the glass may be drawn with a stylus. Then the object is either dipped in dilute hydrofluoric acid for a while or set over a leaden dish which contains a mixture of sulphuric acid and calcium fluoride kept slightly warm by a low flame. Only the places where the coating was removed are attacked, so that, when the latter is subsequently taken off (by turpentine or alcohol), the etch-figure is visible.

MOISSAN has proven that glass is also attacked by perfectly dry hydrofluoric acid gas.

The *formula of hydrofluoric acid* is  $\text{HF}$ , which can be determined in exactly the same way as was done for the analogous chlorine and bromine compounds.

#### Compounds of the Halogens with each other.

54. The halogens, or salt-formers, i.e. the elements fluorine, chlorine, bromine and iodine, (so-called because they form salts with metals by direct combination) can unite with each other to form rather unstable compounds. We shall pass over them with a brief description.

When chlorine gas is led into bromine which is cooled below  $10^\circ$ , a dark-red volatile compound of the formula  $\text{ClBr}$  is formed. With iodine chlorine forms two compounds,  $\text{ICl}$  and  $\text{ICl}_3$ , both of which can be obtained by synthesis. Whether the first or the second is produced depends on the relative amount of chlorine employed.

$\text{ICl}$  is a reddish-brown oil, which slowly solidifies to crystals, that melt

at 24.7°. It boils at 101.3°. Water readily decomposes it to iodic acid, iodine and hydrochloric acid.

**ICl<sub>3</sub>, iodine trichloride**, can be obtained not only by direct synthesis, but also from iodic acid and strong hydrochloric acid and again by the action of PCl<sub>5</sub> on I<sub>2</sub>O<sub>5</sub>. It crystallizes in long yellow needles and decomposes very easily into ICl and Cl<sub>2</sub>. This decomposition begins as low as 25°. In a small quantity of water it dissolves almost without change; larger quantities of water serve to partially break it up, forming hydrochloric and iodic acids.

**IF<sub>5</sub>, iodine pentafluoride**, is produced by the action of iodine on silver fluoride. It is a colorless, strongly fuming liquid.

### Oxygen Compounds of the Halogens.

With the exception of fluorine, the halogens are known to form various oxygen compounds, having the common property of instability, i.e. of being easily decomposed. Most of them can combine with water, forming acids. Oxides which show this latter property are called **acid anhydrides**. The acids which are thus formed from the halogen oxides contain each but one hydrogen atom, and this can be replaced by a metal. Acids containing one hydrogen atom which can be thus substituted are called **monobasic**.

#### HYPOCHLOROUS OXIDE. CHLORINE MONOXIDE, Cl<sub>2</sub>O.

55. This compound can be prepared by passing chlorine over dry mercuric oxide at a low temperature:

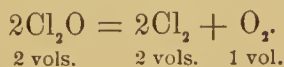


Hypochlorous oxide is a brownish-yellow gas at ordinary temperatures. It can be condensed by strong cooling to a dark-brown liquid, which boils at + 5°. It is an extremely dangerous substance, especially in the liquid state, since the slightest mechanical disturbances make it explode vigorously, breaking up into its elements. It is possible to distill it without decomposition, only when everything with which it comes in contact is entirely free from dust (organic matter). It acts upon sulphur, phosphorus and compounds of carbon with explosive violence.

The *composition* of this compound was determined by BALARD in the following way: He introduced 50 vols. of the gas into a



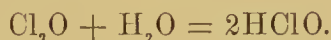
tube over mercury and decomposed it by gently warming. He thus obtained a mixture of chlorine and oxygen which occupied somewhat less than 75 vols. After the chlorine was removed by caustic potash, 25 vols. remained, i.e. 50 vols. chlorine were present, the slight difference which was observed being ascribable to the fact that a little chlorine had united with the mercury in the tube. 1 vol. hypochlorous oxide yielded therefore 1 vol. chlorine and  $\frac{1}{2}$  vol. oxygen. This indicates the formula  $\text{Cl}_2\text{O}$ .



The vapor-density of the compound was found to be 3.03 (air = 1), or 43.63 (O = 16). Its molecular weight therefore becomes 87.26, corresponding to the formula  $\text{Cl}_2\text{O}$  (2Cl = 71; O = 16; sum = 87).

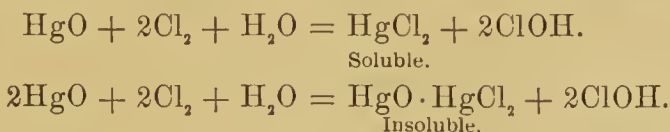
#### HYPOCHLOROUS ACID, $\text{HClO}$ .

56. When chlorine monoxide,  $\text{Cl}_2\text{O}$ , is passed into water, it is absorbed; the solution contains hypochlorous acid:



This compound is known only in aqueous solution. Its composition is studied in its salts.

The same aqueous solution can also be obtained by adding finely powdered mercuric oxide to chlorine water. Distillation may be employed to purify the solution of the acid. Another method is to add at once enough mercuric oxide to form the oxychloride,  $\text{HgO} \cdot \text{HgCl}_2$ , which is insoluble in water and can be removed from the hypochlorous acid solution by filtration:

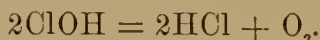


Still another method of preparing the acid solution is to lead chlorine into the solution of a base, e.g. potassium hydrate, at the ordinary temperature, whereupon a salt of hypochlorous acid (hypochlorite) is formed.

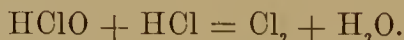


By carefully treating the hypochlorite with the equivalent amount of nitric acid the hypochlorous acid is set free and can be separated from the salts by distillation.

When concentrated, the aqueous solution of hypochlorous acid has a golden color. It is unstable; only dilute solutions can be distilled without decomposition. It oxidizes vigorously, breaking up into oxygen and hydrochloric acid :



On the addition of hydrochloric acid all the chlorine of both compounds is set free:



The hypochlorites act just like the free acid, since the presence of very weak acids, e.g. the carbonic acid of the air, serves to liberate hypochlorous acid. They are therefore extensively employed as bleaching agents (§ 27). A solution of sodium hypochlorite (*eau de Javelle*) is used for this purpose, but chloride of lime ("bleaching powder," § 258) deserves particular notice. The latter is obtained by treating lime with chlorine at ordinary temperatures. The bleaching action of hypochlorous acid is twice as great as that of the chlorine which it contains would be, if the latter were to act in the free state:

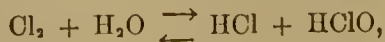


However, it should be remembered that *two* atoms of chlorine were necessary to form the *one* HClO molecule:



On shaking an aqueous solution of hypochlorous acid with mercury a brownish-yellow precipitate of mercuric oxychloride,  $n \text{HgO} \cdot \text{HgCl}_2$ , is formed, which is insoluble in hydrochloric acid. Chlorine water, on the other hand, when shaken with mercury, gives white mercuric chloride,  $\text{HgCl}_2$ , (sublimite). These reactions enable us to distinguish between the two substances.

In a dilute aqueous solution of chlorine we have the following equilibrium:



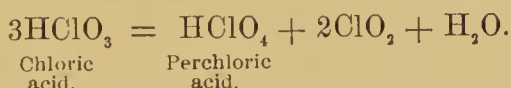
as is shown by the facts that the solution reacts distinctly acid toward lit-

mus and that the hypochlorous acid can be separated from the hydrochloric acid by distillation.

The difference in the action of chlorine water and a solution of hypochlorous acid on mercury is due to the fact that in the above equilibrium the system  $\text{Cl}_2 + \text{H}_2\text{O}$  is far superior to the other.

#### CHLORINE DIOXIDE, $\text{ClO}_2$

57. This gas is formed when potassium chlorate,  $\text{KClO}_3$ , is treated with concentrated sulphuric acid. Chloric acid is at first set free and this decomposes as follows:



Chlorine dioxide is a dark-yellow gas. It can be condensed to a liquid, which boils at  $9.9^\circ$  and solidifies at  $-79^\circ$  to a yellow crystalline mass. It has a peculiar odor resembling chlorine and burned sugar.

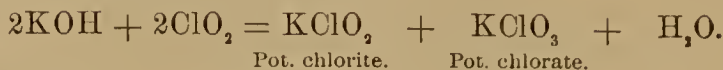
Chlorine dioxide is extremely explosive; warming, jarring or contact with organic substances make it explode with violence. Light slowly decomposes it.

The following experiments give one an idea of the vigor with which it causes oxidation. (1) When finely powdered sugar is mixed carefully with potassium chlorate and a drop of concentrated sulphuric acid is added, the whole mass bursts into flame. The chlorine dioxide set free makes the sugar burn at ordinary temperature. (2) Place a few pieces of yellow phosphorus and some crystals of potassium chlorate under water and allow a few drops of concentrated sulphuric acid to flow down on the two substances. The phosphorus at once burns under water with a brilliant light.

Chlorine dioxide is soluble in water. Such a solution can be easily prepared by floating a little porcelain cup in a large crystallizing-dish with a flat brim and containing 220 c.c. water, putting into the cup 12 g. potassium chlorate and adding a cooled mixture of 44 c.c. concentrated sulphuric acid and 11 c.c. water. The crystallizing-dish is then covered with a glass plate. The chlorine dioxide evolved dissolves in the water, forming a yellow solution.

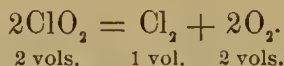
As the quantity of gas obtained from 1-3 g. potassium chlorate is sufficient to kill the bacteria in 1 c.m. ordinary drinking-water, this means has been proposed for purposes of practical sterilization.

When a base is added to a chlorine dioxide solution, a chlorite (§ 58) and a chlorate are formed:



This reaction proceeds very slowly in dilute solution.

The *composition* of chlorine dioxide was determined by GAY LUSSAC as follows: He allowed the gas to flow through a capillary tube with three bulbs. By heating the part of the tube in front of the bulbs he decomposed the gas, the action being non-explosive in so narrow a space. Thus there was obtained in the bulbs a mixture of oxygen and chlorine in the same proportions as they are contained in the compound. The chlorine was absorbed by potash and the remaining oxygen was passed over into a gas-measuring tube. The capacity of the bulbs being known, it was possible from these data to calculate the volume-ratio of oxygen and chlorine. It was found that 100 vols. of the oxide yields 67.1 vols. oxygen and 32.9 vols. chlorine. This ratio is very close to that of 1 : 2, represented by the formula  $\text{ClO}_2$ :



This formula is also confirmed by the vapor-density, which was found to be 34.5 at  $10.5^\circ$ , while the formula  $\text{ClO}_2$  demands  $\frac{35.5 + 2 \times 16}{2} = 33.7$ .

#### CHLOROUS ACID, $\text{HClO}_2$ .

58. This acid is unknown in the pure state. Its sodium salt is formed by the action of sodium peroxide solution on a chlorine dioxide solution:



The silver salt,  $\text{AgClO}_2$ , is a yellow crystalline powder, as is also the lead salt,  $\text{Pb}(\text{ClO}_2)_2$ ; they are both difficultly soluble in water, and break up even on warming to  $100^\circ$  in an explosive manner. The anhydride of chlorous acid, corresponding to the formula  $\text{Cl}_2\text{O}_3$ , is not known.

CHLORIC ACID,  $\text{HClO}_3$ .

59. The chlorates of potassium or barium are the usual starting-points for the preparation of chloric acid. When dilute sulphuric acid is added to the solution of the barium chlorate, barium sulphate is precipitated and a dilute solution of chloric acid is obtained, which may be filtered off from the sulphate and dried in a vacuum desiccator over concentrated sulphuric acid. In this way a 40% solution of the acid may be obtained. On concentrating it any farther, decomposition takes place, oxygen being evolved and perchloric acid formed. The concentrated acid is a powerful oxidizing agent; wood or paper ignite when brought in contact with it. It oxidizes hydrochloric acid, chlorine being given off; farther sulphuretted hydrogen, sulphurous acid and others, even in dilute solution. The following reaction is very characteristic of chloric acid: When indigo solution is added to a dilute solution of the acid, the former is not decolorized; however, on the addition of a little sulphurous acid the color disappears, since the chloric acid is thereby reduced to lower oxides.

The *salts* are all soluble in water, that of potassium being somewhat difficultly so, however.

The *composition of chloric acid* was ascertained by STAS from an analysis of silver chlorate. An accurately weighed amount of the latter was reduced by a solution of sulphurous acid to silver chloride and this was filtered off and weighed. Since he knew from previous investigations the exact composition of silver chloride, the analysis of the silver chlorate was complete. STAS found thus that silver chlorate consists of:

Silver.....	56.3948%
Chlorine.....	18.5257%
Oxygen.....	25.0795%
Total.....	100.0000%

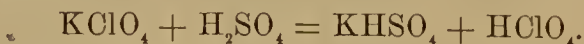
The atomic weight of silver is 107.93; that of chlorine 35.45; that of oxygen 16.0. We then find that the ratio of the atoms in this salt is

$$\frac{56.3948}{107.93} = 0.52; \quad \frac{18.5257}{35.45} = 0.52; \quad \frac{25.0795}{16.00} = 1.58;$$

very close to 1 : 1 : 3, from which it follows that the empirical formula of the salt is  $\text{AgClO}_3$ , that of the acid itself  $\text{HClO}_3$ .

#### PERCHLORIC ACID, $\text{HClO}_4$ .

60. This compound is obtained by distilling potassium perchlorate with an excess of sulphuric acid of 96–97.5% in vacuo:



Pure perchloric acid boils at  $39^\circ$  under a pressure of 56 mm. Hg, and has a specific gravity of  $D_4^{22} = 1.764$  at  $22^\circ$ . It is a colorless liquid which does not solidify on being cooled with solid carbon dioxide and alcohol (about  $-80^\circ$ ). It decomposes slowly, taking on a dark color. With one molecule of water it forms a crystallized compound, which melts at  $50^\circ$ ; with still more water a thick oily liquid is formed, similar to concentrated sulphuric acid. Such an acid contains 71.6%  $\text{HClO}_4$ ; it distills constant at  $203^\circ$  and has a specific gravity of 1.82. The dilute solution of the perchloric acid is stable.

In the concentrated state perchloric acid is a very strong oxidizing agent. When a little is dropped on wood or paper, these ignite with explosion. Very painful flesh-wounds are produced by it. When dilute, it does not, however, release its oxygen nearly so readily as chloric acid. It can, for example, be gently warmed with hydrochloric acid without giving off chlorine, and it is not reduced by sulphurous acid. By these facts and by its yielding no chlorine dioxide with sulphuric acid it may be distinguished from chloric acid.

The salts of perchloric acid, perchlorates, are all soluble in water; that of potassium and especially that of rubidium are, however, very difficultly soluble in cold water.

The *composition* of perchloric acid has been determined, as in the case of chloric acid, by the analysis of a salt, in this instance the potassium salt. A weighed amount of the latter is heated to drive off all the oxygen. The loss in weight indicates the amount of the latter. The analysis of the remaining potassium chloride,  $\text{KCl}$ , shows the amounts of potassium and chlorine. From these data it is found, in the same manner as with chloric acid, that the empirical formula of the salt is  $\text{KClO}_4$ , that of the acid, therefore,  $\text{HClO}_4$ .

Chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ , is the oxide corresponding to perchloric acid :



It may be obtained by slowly adding perchloric acid to phosphorus pentoxide cooled below  $-10^\circ$ . By distillation on a water bath the oxide is obtained as a colorless liquid, which boils at  $82^\circ$ . It is more stable than the other oxides of chlorine ; it neither attacks paper nor acts on sulphur or phosphorus in the cold.

#### OXYGEN COMPOUNDS OF BROMINE.

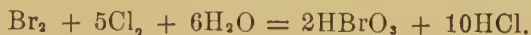
61. Although no compounds with oxygen alone are known, there are two oxygen acids, viz., hypobromous and bromic.

Hypobromous acid,  $\text{HBrO}$ , can be obtained in the same way as  $\text{HClO}$ , namely, by shaking up bromine water and mercuric oxide together. The dilute solution can be distilled in vacuo, and has properties entirely analogous to those of hypochlorous acid.

Bromic acid,  $\text{HBrO}_3$ , can be obtained from the barium salt with sulphuric acid or from the silver salt with bromine water :



It is also formed when chlorine is passed into bromine water :



It corresponds in its conduct with chloric acid. Many reducing agents, such as hydrogen sulphide and sulphurous acid, are able to withdraw all its oxygen. Most of its salts are difficultly soluble in water. When heated, they give up all their oxygen.

#### OXYGEN COMPOUNDS OF IODINE.

62. When iodine is introduced into a cold dilute solution of caustic potash or soda, a colorless liquid is obtained, which has other properties when fresh than it has later. When freshly prepared it decolorizes indigo solution and iodine is liberated on the addition of very weak acids. Later on these two properties disappear. It is therefore to be supposed that a hypo-iodate  $\text{KIO}$  is first formed and that this is changed slowly to  $\text{KI}$  and  $\text{KIO}_3$ . At the boiling-point the change takes place almost immediately.

Iodine pentoxide,  $\text{I}_2\text{O}_5$ , is the anhydride of iodic acid, since it can be obtained by heating this acid to  $170^\circ$ ,

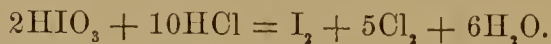


and yields the same acid when dissolved in water. It is a white crystalline substance, which breaks up into its elements at 300°.

**Iodic acid**,  $\text{HIO}_3$ , is best prepared by the oxidation of iodine with nitric acid:



Iodic acid is crystalline and easily soluble in water. It is a powerful oxidizing agent, setting free chlorine from hydrochloric acid, for example:

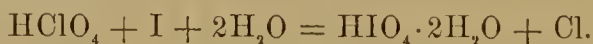


It reacts instantaneously with hydriodic acid, all the iodine of both compounds being precipitated:



The salts of this acid, the *iodates*, are in general not very soluble in water; however, those of the alkali metals dissolve rather easily.

**Periodic acid**,  $\text{HIO}_4 + 2\text{H}_2\text{O}$ , is formed by the action of iodine on perchloric acid:



It is a colorless crystalline solid that is entirely decomposed at 140° into iodine pentoxide, oxygen and water (§ 145).

### NOMENCLATURE.

63. The system of naming the various halogen **oxygen-acids** is a general one, which is also used for the acids of other elements. The best-known acid usually has the suffix *-ic*, e.g. chloric acid, phosphoric acid, sulphuric acid, etc. Acids that contain more oxygen have in addition the prefix *per-*, thus perchloric acid and persulphuric acid. Acids containing less oxygen have the suffix *-ous*, e.g. chlorous acid, sulphurous acid, phosphorous acid, etc. Those which contain still less oxygen have the suffix *-ous* and also the prefix *hypo-*, e.g. hypochlorous acid, hyposulphurous acid and hypophosphorous acid.

The names in use in pharmaceutical chemistry (see the National Pharmacopœia) follow the Latin. Thus we have *Acidum sulphuricum* (sulphuric acid) and *Acidum sulphurosum* (sulphurous acid).

The names of the **salts** of the best-known (*-ic*) acids end in



*-ate*, e.g. potassium chlorate, -sulphate, -phosphate. The salts of the *-ous* acids have the ending *-ite*, as potassium chlorite, -sulphite, -phosphite. The salts of *hypo-ous* acids are called *hypo-ites*; thus sodium hypochlorite, -hyposulphite, -hypophosphite.

The names of the anhydrides correspond to those of their acids.

In naming **oxides** the name of the element with or without the ending *-ic* is used, unless there is more than one oxide. Where there are two oxides, the name of the one with the more oxygen ends in *-ic*, that of the other in *-ous*, e.g. mercuric oxide, arsenic oxide, mercurous oxide, arsenious oxide. An oxide with less oxygen than the *-ous* compound is given the prefix *hypo-*, and one with more than the *-ic* oxide the prefix *per-*, as in the case of acids, thus hypochlorous oxide, lead peroxide. In some cases, for the sake of euphony, the suffix is added to the Latin instead of the English stem, as cuprous, ferric, etc.

For historical reasons many names now in use do not conform to this system. In some instances the oxide first discovered took the suffix *-ic*, and those subsequently discovered were named accordingly, as in the case of the nitrogen oxides (§ 119).

It is not uncommon to speak of oxides of the general formula  $M_2O_3$  as *sesquioxides*.

A much more rational system is to indicate the number of atoms of oxygen by the Latin or Greek numeral, e.g. chlorine protoxide, or monoxide, iodine pentoxide, etc.

### SUMMARY OF THE HALOGEN GROUP.

64. It is evident from the foregoing descriptions that the properties of the halogens and their compounds possess great similarity among themselves. A closer study reveals the fact that the increase of atomic weight is accompanied by a gradual change of physical and chemical properties. Let us notice the physical properties, for example :

	F.	Cl.	Br.	I.
Atomic weight.....	19	35.45	79.96	126.85
Melting-point.....	—	—102	— 7	+ 113
Boiling-point.....	—	— 33	+ 63	+ 200
Sp. g. (liquid or solid)..	—	1.33	3.18	4.97
Color.....	{ pale green- ish yellow.	greenish yellow.	brown.	violet black.

It is seen that the values of the physical constants increase on the whole with the atomic weight. The purely metalloidal character of the first three is also found in iodine, although in the case of the latter an external characteristic of metals, viz., metallic lustre, is at once noticeable.

The affinity for hydrogen decreases as the atomic weight increases. We saw that fluorine combines with this element even in the dark and at very low temperatures in an explosive manner; iodine unites with hydrogen directly only at a high temperature and the compound is easily decomposed by heat. Inversely the oxygen compounds are the more stable the higher the atomic weight of the halogen. While a halogen of a low atomic weight displaces a halogen of higher atomic weight from its hydrogen compound, e.g.



the halogen with higher atomic weight can on the other hand replace one with lower in its oxygen compounds, setting that other one free:



### ELECTROLYTIC DISSOCIATION.

65. In § 30 it was stated that the properties of dry hydrogen chloride differ widely from those of an aqueous solution of this gas. It was also stated there that many substances undergo a similar change of properties when they are dissolved in water. We may now consider the nature of this change.

If we investigate the freezing-point depression of the aqueous solution of an acid, base or salt of known concentration, we find that the depression does *not* correspond with the theoretical calculation (§ 43). The freezing-point depression and the boiling-point elevation are greater than they should be. A 1% sodium chloride solution would, for example, be expected to show a depression of  $\frac{19}{58.5} = 0.325^\circ$ , the molecular depression for water (§ 43) being 19, i.e.  $AM = 19$ , and the molecular weight of sodium chloride 58.5. In reality, however, the depression is found to be 1.9 times as great, namely,  $0.617^\circ$ . As the osmotic pressure is proportional to the freezing-point depression (§ 42), it must also be greater than the calculated amount.

An analogous phenomenon is observed in the case of gases. In quite numerous instances the pressure exerted by a definite weight of gas occupying a definite volume at a definite temperature is greater than the calculation indicates. This is explained by assuming a breaking up of the gas molecules; the number of particles free to move about thus increases and accordingly the pressure becomes greater. This phenomenon is known as *dissociation* (§ 49).

In the case of the abnormal osmotic pressure one is led to a similar explanation by assuming that the molecules are split up into several independent particles. A difficulty arises, however, when one considers how such a division is to be conceived. In solutions of salts in water it would be possible to assume a hydrolytic separation, i.e. into free base and free acid (§ 239), which would necessarily be complete in dilute solutions of the salts of strong acids and bases, inasmuch as the osmotic pressure of such solutions in concentrations of  $\frac{1}{10}$  normal (§ 93), for instance, amounts to double the calculated pressure. There are, however, serious objections to such a hypothesis. In the first place, it has never yet been possible to separate such a solution by diffusion into the free base and free acid which it is supposed to contain. A second and still more serious objection is that an acid or base in an aqueous solution by itself exerts an osmotic pressure greater than that calculated. Here, however, hydrolytic dissociation is impossible.

The question as to the real nature of the division has found its answer in a consideration of the relation which exists between the abnormal osmotic pressure and the transmission of the electric current. ARRHENIUS observed that only those substances which conduct the electric current in aqueous solution, namely, acids, bases and salts, show the above-mentioned abnormalities in osmotic pressure. When these substances are dissolved in another liquid than water, the resulting solution is a non-conductor, but its osmotic pressure again assumes the normal. These facts make plain the connection between these apparently very heterogeneous phenomena.

In order to understand this relation it is necessary to know the usual explanation of electrolytic conduction. Let us consider hydrochloric acid as an example. Perfectly dry hydrochloric acid

gas is a non-conductor, as is also perfectly pure water. However, when the gas is dissolved in water, a solution is obtained which transmits electricity very well. Evidently a certain reaction must have taken place between the water and the hydrogen chloride. We were led to surmise this above (§ 29), when it was found that this gas solution does not obey HENRY'S law. Since during the transmission of the current the hydrogen chloride is broken up into hydrogen and chlorine while the water remains unchanged, it must be assumed the hydrogen chloride molecules are the ones which have undergone a change.

The phenomena of electrolytic conduction now find their complete explanation in the assumption that the change which the hydrochloric acid underwent consisted in a separation of its molecules into electrically charged atoms (*ions*). This separation may have been complete or partial, the extent depending upon the concentration among other things. When a current passes through the solution, the negatively charged chlorine ions (the *anions*) are drawn toward the positive electrode (a *n o d e*); they become electrically neutral on contact with the latter and escape from the liquid. Similarly the positively charged hydrogen ions (*cations*) wander toward the negative electrode (c a t h o d e). In this way conduction goes on, the undivided molecules having no part in it. This separation of the molecules is known as **electrolytic dissociation**, or **ionization**.

In order that this hypothesis may also account for excessive osmotic pressure, it must be assumed that the ions are independent particles, just as free to move as the molecules are supposed to be. The number of freely moving particles in the same volume is thus increased. Hence, whether the amount of ionization is calculated from the electrical conductivity or from the osmotic pressure, the result should be the same in so far as the above hypothesis is true. This is in reality the case.

Supposing, namely, that every molecule yields  $n$  ions by the dissociation and that the dissociated portion of the whole number of molecules is  $\alpha$ , the number of freely moving particles is

$$1 - \alpha + n\alpha = 1 + \alpha(n - 1).$$

The osmotic pressure must therefore be  $[1 + \alpha(n - 1)]$  times greater

than in the case of undivided molecules. If this pressure  $p$  is  $p_0$  in the latter case, then

$$p = p_0[1 + \alpha(n - 1)];$$

wherefore

$$\alpha = \frac{p - p_0}{(n - 1)p_0} \dots \dots \dots (1)$$

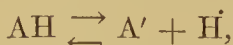
From the electrical conductivity we are able to find the value of  $\alpha$  in the following way: As the dilution becomes greater, the *molecular conductivity* increases. This is the specific conductivity of the solution multiplied by the number of liters in which a gram-molecule of the substance is dissolved. As the dilution is gradually increased, the molecular conductivity approaches a definite limit. Since the conductivity is only due to the dissociated molecules, it may be assumed that, when this limit is reached, all molecules are divided into ions. If the molecular conductivity for infinite dilution is represented by  $\lambda_\infty$  and that for the dilution  $v$  (1 gram-molecule in  $v$  liters) by  $\lambda_v$ , it is evident that

$$\alpha = \frac{\lambda_v}{\lambda_\infty} \dots \dots \dots (2)$$

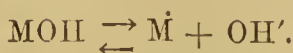
Below are given several values of  $\alpha$ , calculated from the observed freezing-point depression ( $\alpha_v$ ) and from the conductivity ( $\alpha_e$ ) of solutions of the respective salts, in order to show the agreement of the values found in the two ways. The figures are for solutions containing 1 g. substance dissolved in a liter.

	KCl.	NH <sub>4</sub> Cl.	KI.	NaNO <sub>3</sub> .
$\alpha_v$	0.82	0.88	0.90	0.82
$\alpha_e$	0.86	0.84	0.92	0.82

66. In a case of electrolytic dissociation we have a state of equilibrium to deal with, namely, that between the undissociated molecules on the one hand and the ions on the other; an equilibrium which in the case of a monobasic acid may be represented by



where  $A'$  is the acid radical (anion) and  $H$  the hydrogen ion (cation). For a base we have



We may apply here the equilibrium equation deduced in § 49.

Given  $a$  gram-molecules of  $AH$  per unit-volume, of which  $x$  are divided into two ions each, then the equilibrium is represented by

$$a - x = Kx^2.$$

From this equation it necessarily follows that *the dissociation is diminished* (just as in the case of hydrogen iodide gas) *by the introduction into the solution of a substance with like ions.* This effect may be produced on a salt in solution by the addition of a salt of the same base or a salt of the same acid to the solution. The equation then becomes:

$$a - x = K \cdot x(x + p),$$

$p$  being the concentration of the added ion.  $K$  can only remain constant provided  $x$  diminishes.

It also follows that *the degree of dissociation depends on the concentration.* If the latter be increased  $n$ -fold, we have from the above equation

$$n(a - x) = Kn^2x^2, \quad \text{or} \quad (a - x) = K \cdot n \cdot x^2.$$

If  $n$  is  $> 1$ ,  $x$  must diminish, i.e. *the ionization decreases with increasing concentration.* If  $n$  is  $< 1$ ,  $x$  must increase, i.e. *the ionization increases with the dilution.* When  $n$  is infinitely small, we have

$$a = x,$$

in other words, *at infinite dilution the ionization is complete.*

We are now able to give another definition of acids and bases than that of § 30. *Acids are those substances which give H-ions in aqueous solution; bases under the same condition give OH-ions.*

All the properties of acids, bases and salts are closely connected with the degree of their ionization,—among others that which is indicated by the rather vague term “strength” of an acid or base. Experience has taught that those acids and bases are strongest which are the most ionized for the same dilution. Hydrochloric acid is, for example, stronger than hydrofluoric acid. At a dilution of one gram-molecule per liter the former is almost completely (about 80%) split up into ions, the latter only 3%.

It was remarked above (§ 30) that acids turn blue litmus red, and bases red litmus blue. It is only natural to seek the cause of

these common properties of acids on the one hand and bases on the other in that which all acid solutions have in common, namely, hydrogen ions, and in that which all solutions of bases have in common, namely, hydroxyl ions. The reactions between acids, bases and salts in aqueous solution are almost invariably reactions between their ions. We shall explain this later in many instances; the following example may suffice for the present. When dilute solutions of a base and an acid are mixed, we have a salt solution (§ 30). In order to understand what reaction has taken place we must know that in dilute solution most salts are almost wholly split up into ions. Water itself, however, is split up only in an extremely small amount. In the equilibrium



there is thus very little of the system on the right-hand side. Now, when a base and an acid are mixed, we have together in the solution  $\text{M} + \text{OH}'$  and  $\text{A}' + \text{H}$ . Of these ions  $\text{M}$  and  $\text{A}'$  can exist freely side by side; but not so with  $\text{H} + \text{OH}'$ , for these must unite to form water according to the above equilibrium. In the formation of the salt we therefore have only the  $\text{H}$  and  $\text{OH}'$  ions uniting, producing undissociated molecules of water.

When *ARRHENIUS* presented the doctrine of electrolytic dissociation in 1887, it met at first with much opposition. It was seen that its effect would be to produce a veritable revolution of many previously accepted views. Compounds such as hydrochloric acid, sodium nitrate and others, which had ever been considered as the most stable, were to be supposed according to the theory of *ARRHENIUS* to break up as soon as they dissolve in water. It also seemed nonsensical that we should have to assume the existence of free potassium and iodine in a solution of potassium iodide, for example, since potassium produces hydrogen and potassium hydroxide as soon as it touches water and since a *KI* solution is colorless, while iodine solutions are brown.

So far as the first point is concerned, it should be noted that it is the solutions of these same strongly ionized compounds which are chemically the most active, a fact which indicates rather a loose than a firm union of the constituent atoms in the molecules. In

regard to the example of potassium iodide solution and other cases, care must be taken not to confuse atoms and ions. The solution of potassium iodide—retaining our illustration—contains neither free potassium nor free iodine but *ions of potassium* and *ions of iodine*. The atoms, however, must possess an altogether different energy-supply than the ions whose electric charges are very heavy, as can be proved by different methods. It is this *energy-supply* on which the properties of bodies depend; and since this is apparently entirely different with the ions than with the atoms, it is perfectly natural that the latter should display other properties than the former.

### SULPHUR.

67. Sulphur was known to the ancients. It occurs free in nature, principally in the vicinity of active or extinct volcanoes. Sicily is its most important locality, but large quantities are also found in Iceland, Japan, the United States (Yellowstone Park) and Mexico. It is separated from the accompanying rock, or matrix, by fusion.

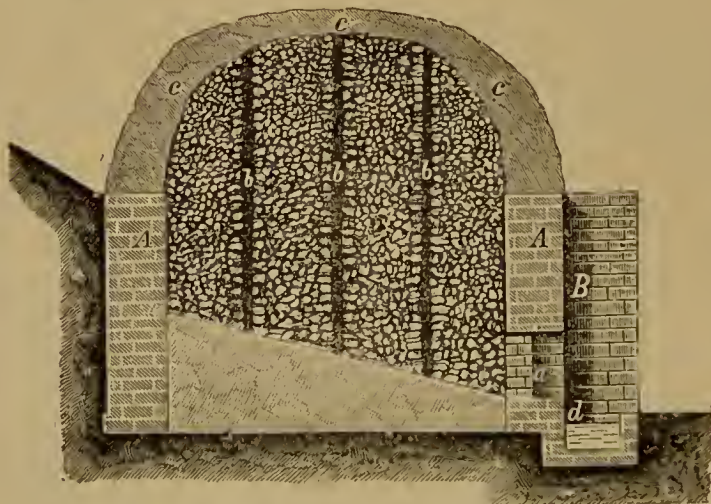


FIG. 28.—EXTRACTION OF SULPHUR.

**Extraction.**—In Sicily this has been done for centuries in a rather crude manner, the sulphur itself being used as fuel, whereby about one-half is lost. Fig. 28 represents a vertical section of a kiln. The latter is built in the side of a hill, as indicated, and the ore is piled up in it so that air-passages (*b*) remain open. The entire heap is then covered with powdered ore (*c*) and on top of this with some calcined ore, by which means the entrance and circulation of air is largely prevented. This heap (calcarone) is ignited



below; a part of the sulphur burns and the heat that it generates is sufficient to melt the rest, which flows out at (*a*) and is collected in (*d*).

**Refining.**—The sulphur thus obtained is still impure, containing among other substances about 3% of sand. It is refined (Fig. 29) by distillation. The crude sulphur is melted in *B*, whence it is let down into the cast-iron cylinder *A*, which is heated to a temperature above the boiling-point of sulphur. The vapor is conducted into a large brick chamber, equipped with a safety-valve for the release of air. If the distillation is carried on so slowly that the temperature of the chamber does not exceed the melting-

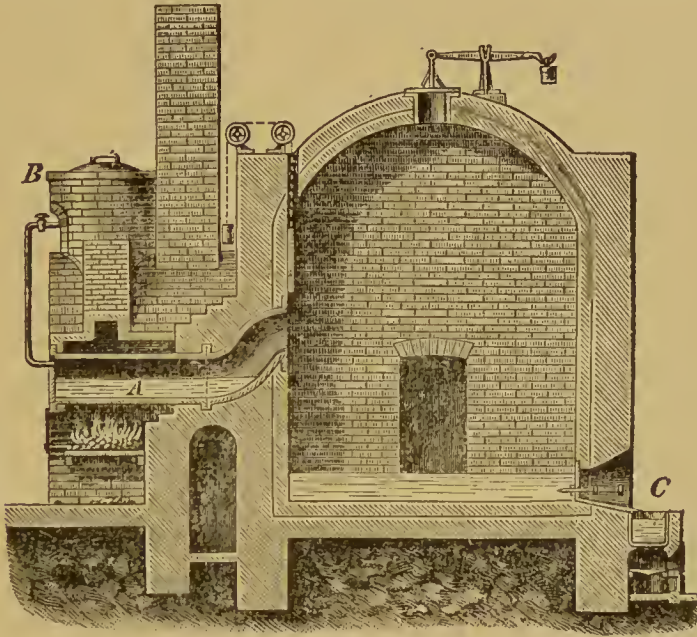
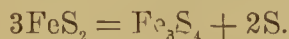


FIG. 29.—DISTILLATION OF SULPHUR.

point of sulphur, the latter is deposited in the form of a fine powder, called "*flowers of sulphur*"—just as water vapor, when suddenly cooled below  $0^{\circ}$ , turns to snow. Rapid distillation, however, yields a layer of liquid sulphur on the floor. It may be let out through the opening *C* and cast into slightly conical wooden molds. This is the roll sulphur, or *roll brimstone* of commerce.

Besides occurring in the free state sulphur is also found in numerous compounds, from some of which it is obtained, e.g. pyrite, or iron pyrites,  $\text{FeS}_2$ , which yields sulphur on heating:



Many other compounds of the element with metals, the sul-

phides, occur in nature, e.g. *galenite* (lead sulphide), *zinc blende* (sphalerite, zinc sulphide), *stibnite* (antimony sulphide), *cinnabar* (mercury sulphide), *realgar* and *orpiment* (arsenic sulphides) and *chalcopyrite* (copper pyrites, copper and iron sulphide). Sulphur also occurs in the natural sulphates, of which *gypsum* ( $\text{CaSO}_4 + 2\text{H}_2\text{O}$ ) is the most important. It is also found in the organic world as a constituent of the albuminoids.

*Physical Properties.*—Sulphur can appear in various forms. At ordinary temperatures the stable form is a yellow crystalline solid; melting-point,  $114.5^\circ$ ; boiling-point,  $450^\circ$ . A little above its melting-point sulphur is a mobile yellow liquid. With a continued rise of temperature it becomes much darker in color and very viscid; at  $250^\circ$  it can no longer be poured; above  $300^\circ$ , however, it again becomes mobile, the dark color remaining; at  $450^\circ$  it boils, producing an orange-colored vapor. During cooling these phenomena reappear in inverse order.

Sulphur is insoluble in water and difficultly soluble in alcohol and in ether; it is easily soluble in carbon bisulphide and in sulphur monochloride,  $\text{S}_2\text{Cl}_2$ . 100 parts  $\text{CS}_2$  dissolve 46 parts S at  $22^\circ$ .

The *molecular weight* of this element, more than that of any other, depends on the temperature. Sulphur dissolved in carbon bisulphide and in fused naphthalene possesses, according to the determination of the boiling-point elevation and the freezing-point depression, the molecular formula  $\text{S}_8$ . In the gaseous state the density (air = 1) varies from 7.937 at  $467.9^\circ$  to 2.23 at  $860^\circ$  and

Pressure in mm. Mercury.	Vapor-density (air = 1).	Vapor-density corresponding to
14.0	4.85	$\text{S}_4 = 4.43$
20.5	6.08	$\text{S}_5 = 5.54$
39.1	6.60	$\text{S}_6 = 6.65$
81.6	7.51	$\text{S}_7 = 7.75$
104.2	7.63	$\text{S}_8 = 8.86$
539.2	7.89	

then remains constant even as high as  $1040^\circ$ , indicating that at the lowest temperatures sulphur vapor consists of  $\text{S}_8$  molecules, and at  $860^\circ$  of only  $\text{S}_2$  molecules. At the boiling-point of sulphur

(450°) the vapor-density is found to vary with the pressure as shown in the table.

This shows that the vapor-density increases rapidly at low pressures and slowly when the pressure becomes higher than about 100 mm. However, the increase is continuous. It may therefore be concluded that the dissociation of  $S_8$  molecules into  $S_2$  molecules proceeds steadily till it is complete, and that at intermediate intervals the vapor is a mixture of  $S_2$  and  $S_8$ .

68. *Allotropic Modifications.*—The ability of sulphur to form molecules of very different number of atoms is probably the reason why it exists in several allotropic conditions. At least four solid forms are known, while in the liquid state the viscid modification may also be considered as an allotropic form. The solid allotropic conditions can be divided into crystallized and amorphous. Sulphur is dimorphic, forming *rhombic* as well as *monoclinic* crystals. The former are transformed into the latter on heating.

Rhombic sulphur can be obtained in beautiful crystals by allowing a solution of sulphur in carbon bisulphide or chloroform to slowly evaporate. Monoclinic sulphur is easily obtained in the following manner: Some sulphur is fused in a large crucible and allowed to cool slowly until a crust forms on the surface. The crust is then broken through and the liquid sulphur poured out; the sides of the crucible are found to be covered with long, yellow transparent needles. In the course of a few hours these become opaque and brittle, however, and crumble at the slightest touch to a powder, that consists of rhombic crystals.

Amorphous sulphur can be obtained in two ways, the properties of the two products being unlike. Thus we have an amorphous sulphur *soluble*, and another *insoluble*, in carbon bisulphide.

The soluble kind results from the decomposition of certain sulphur compounds. When hydrogen sulphide water is exposed to the air, sulphur slowly separates in the form of a white powder. The polysulphides ( $CaS_n$ ,  $K_2S_n$ , etc.) yield, when decomposed by an acid, a cloudy milk-like liquid, which is found to contain extremely fine particles of amorphous sulphur. In either case there is always formed in addition to the soluble variety some insoluble (in  $CS_2$ ) sulphur.

The insoluble form may be best prepared in the following manner: Sulphur is heated till the viscid stage is reached, and is then poured in a fine stream into cold water, whereby the semi-solid *plastic* modification is formed, which becomes brittle after a time. Sulphur in this state is, excepting a small portion, insoluble in carbon bisulphide. Plastic sulphur

passes gradually over into the rhombic form; at  $95^{\circ}$  the transformation is sudden and accompanied by the evolution of considerable heat.

**69. Chemical Properties.** — Sulphur combines directly with many elements, not only metals but also metalloids. It has been already stated (§ 10) that it burns with a blue flame when heated in air or in oxygen. The halogens and hydrogen unite with it directly. Powdered iron and sulphur, when mixed and heated, combine energetically, producing great heat (§ 20). Copper takes fire in the vapor of boiling sulphur. When mercury and sulphur are rubbed together in a mortar, black  $\text{HgS}$  is formed. The sulphur compounds of the metals are called sulphides.

#### THE TRANSITION-POINT.

**70.** As stated in § 68 sulphur can crystallize in two forms, rhombic and monoclinic. These forms can be readily transformed one into the other. The peculiar phenomena connected with this transition deserve a closer study. At ordinary temperatures sulphur is rhombic and remains so till the temperature  $95.4^{\circ}$  is reached, above which there begins a slow but complete transformation into the monoclinic form. Inversely, when the monoclinic modification is subjected to a temperature below  $95.4^{\circ}$ , a complete change into the rhombic form occurs. At the temperature named the two modifications are equally stable and can exist side by side in any proportions for an indefinite period; above it only the monoclinic, below it only the rhombic, can exist permanently. Such phenomena are not infrequent. The temperature at which the one system passes into the other is called the **transition-point**, also **point of inversion**. This transition-point possesses great analogy with the melting-point. Just as ice, for example, is changed into water above  $0^{\circ}$  and water into ice below  $0^{\circ}$ , so in a system of substances possessing a transition-point only one system is stable below that point, above it only the other.

The theoretical explanation of both phenomena is exactly the same. Let us consider a body, ice for example, at temperatures slightly below its melting-point, and represent graphically in the diagram  $OTP$  (Fig. 30) the values of the vapor tension corresponding to different temperatures. The result is the line marked *ice* in the figure. This vapor-tension curve, if prolonged through and beyond the melting-point, is found to bend sharply at the

latter and take a new direction. This deflection is very slight in the case of ice and water, but nevertheless capable of experimental proof; it is much plainer with benzene and many other substances. By carefully cooling water it can be made to remain liquid even under  $0^{\circ}$ ; such a liquid is said to be *superfused*. The vapor-tension of this superfused water is greater than that of ice at the same temperature and the curve representing the former is but a continuation of the vapor-tension curve for water. Since the vapor-tension of superfused water is greater than that of ice, water at temperatures below  $0^{\circ}$  must, according to previous conclusions (§ 43, 3), pass into ice, when the two are in contact. However, the vapor-tension of water at a temperature slightly above  $0^{\circ}$  will be less than that of ice and we shall have the ice transformed into water. It is therefore evident that both above and below the melting-point one of the systems will necessarily disappear.

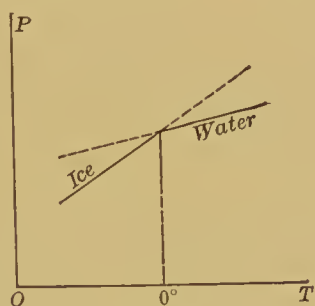


FIG. 30.

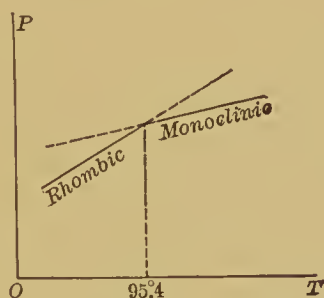


FIG. 31.

Exactly the same explanation can be offered for the *transition-point*. Below  $95.4^{\circ}$  the vapor-tension of rhombic sulphur is less than that of monoclinic; above, the vapor-tension of the rhombic variety exceeds that of the monoclinic. There is therefore a complete transformation from one system to the other when the temperature is other than  $95.4^{\circ}$ , for the same reason as in the case of the melting-point; moreover, just as ice and water under ordinary pressure can exist side by side indefinitely only at  $0^{\circ}$ , so both modifications of sulphur are coexistent only at  $95.4^{\circ}$ , since only then is the vapor-tension equal in both systems (Fig. 31).

Among other methods for the **determination of the transition-point** a convenient one is the *dilatometric method*. It is based on the change of volume (specific gravity) which a body usually undergoes on passing through the transition-point. In measuring this

a dilatometer is used, an instrument which may be compared to a thermometer of very large dimensions. After rhombic sulphur, for example, has been placed in the dilatometer, the latter is filled with a chemically indifferent liquid (kerosene, linseed oil) and put in a large water-bath; the temperature is then slowly raised. Below the transition-point the volume is seen to slowly and steadily increase with the temperature on account of expansion; as soon as the temperature gets a trifle above  $95.4^{\circ}$ , however, a marked increase of volume is observed, although the temperature be maintained constant; thereupon expansion again proceeds gradually, as before, if the temperature is allowed to rise. The marked change of volume indicates the transition of the rhombic sulphur into monoclinic.

#### THE PHASE RULE OF GIBBS.

71. Very many physical and chemical phenomena have been correlated and made easy of comprehension by a theorem which GIBBS has deduced thermodynamically. He calls it the "phase rule." In order to understand its meaning it is necessary to consider first a few definitions.

We may take, for example, a saturated solution of salt and water in a vessel that is closed with a movable piston. Under this solution let there be a little solid salt, above it the vapor of the solution. The salt and the water, of which the system is made up, are called by GIBBS **substances**, i.e. *those components which can combine with each other in variable proportions* (forming in this case a solution). Moreover, the system consists manifestly of three *parts, that can be mechanically separated*; viz., solid salt, solution and vapor. GIBBS terms such parts of a system **phases**. The system under consideration is made up, according to these definitions, of two substances and three phases.

So long as the temperature remains constant, the vapor of the salt solution possesses a definite tension. If we increase the volume by raising the piston, a definite amount of water will evaporate; since the solution was saturated, the result will be that a little salt will be deposited; in the end the quantities of vapor, solution and salt will therefore have altered, but the composition of each phase remains the same. The tension, and hence also the concentration, of the vapor is unchanged, since the temperature

is constant; there is likewise no change in the concentration of the salt solution. The same is true in case the volume be diminished. It therefore follows that the equilibrium of such a system is independent of the quantities of the various phases. An equilibrium of this sort is called by GIBBS a "complete" equilibrium and, since the system is not homogeneous throughout, but consists of three parts which can be mechanically separated, it is termed a **complete heterogeneous equilibrium**. It possesses the following characteristic: At a definite constant temperature the vapor tension is fixed; if it be made even slightly larger or smaller, one of the phases will gradually and completely disappear, provided the temperature remains constant. On increasing the pressure the gaseous phase wholly condenses, so that only solution and salt remain. A decrease of pressure results in the complete evaporation of the solution, vapor and salt only being left.

The same is true when the pressure remains constant and the temperature varies.

An entirely different behavior is shown by a system made up of an unsaturated salt solution and its vapor. At a constant temperature and a definite position of the piston the vapor tension has a definite value, as in the former case. If, however, the volume of vapor be changed, the tension will correspondingly vary, for, if the volume be increased, for example, more water evaporates, the solution becomes more concentrated and the vapor tension of course lessens. Therefore for every definite temperature there are not simply one but infinitely many vapor tensions under which this system can be in equilibrium. The result is that the slightest change of volume or pressure does not necessitate the disappearance of one of the phases. GIBBS calls this sort of equilibrium an **incomplete heterogeneous equilibrium**.

Suppose that a solution of salt that is not quite saturated be put under the piston and the piston slowly raised, the temperature remaining constant. The vapor tension will thereupon steadily decrease till the point is reached when the solution is saturated. Any farther increase of volume has no effect on the vapor tension, because salt at once begins to separate out and the concentration of the solution does not change any more. At the moment the solution becomes saturated the incomplete heterogeneous equilibrium passes over into the complete.

The phase rule may now be expressed thus: *A complete heterogeneous equilibrium exists when  $n$  substances form  $n + 1$  phases. If less phases are present, the equilibrium is incomplete.*

The example of the salt solution illustrates this well. In the case of complete equilibrium there were two substances (water and salt) and three phases (solid salt, solution and vapor); in the case of incomplete equilibrium there were also two substances present, but only two phases.

Let us apply the phase rule to water and to sulphur, in order to see what significance is given to the melting-point and the transition-point by this method of treatment. In both cases we have only one substance; complete equilibrium will therefore exist when two phases are present. In the case of water three phases are possible, namely, ice, liquid and vapor.

In the following graphic representation, Fig. 32, the temperatures,  $t$ , are plotted as abscissæ, the pressures,  $P$ , as ordinates.

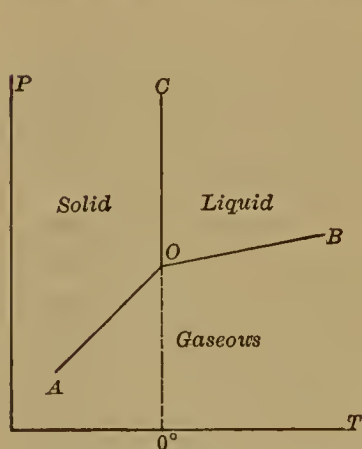


FIG. 32.

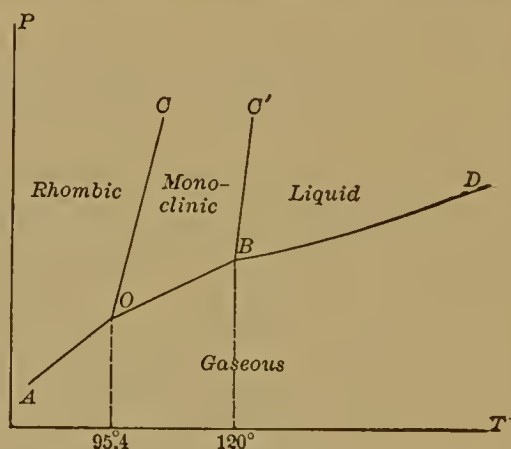


FIG. 33.

Let us first consider liquid water above  $0^\circ$ . To every temperature there corresponds a definite vapor tension. The ordinates of every point in the line  $OB$  indicate these vapor tensions. If the pressure at a certain temperature were greater than that indicated by the ordinate, the gaseous phase would completely disappear. The line  $OB$  therefore represents the boundary between the liquid and gaseous phases for the various temperatures and pressures. Every point in the area  $COB$  represents the liquid, every point in  $AOB$  the gaseous, phase. Only the points of the line  $OB$  indicate the temperatures and corresponding pressures, at which both phases



are coexistent. The line  $OB$  therefore ends on one side at  $0^\circ$ ; its other end is at the critical temperature, since at this point vapor and liquid become identical.—Let us now allow the temperature to fall below  $0^\circ$ . The liquid phase disappears and ice takes its place. The ordinates of the points on the line  $OA$  again give the vapor tensions of ice for different temperatures. For the same reason as above  $OA$  is the boundary-line between the solid and gaseous phases. Only along this line are the two coexistent. The line  $OA$  extends to the absolute zero, since the gaseous phase then disappears.

The melting-point of ice depends somewhat on the pressure, being lowered by increasing pressure  $0.0075^\circ$  per atmosphere. Both phases, ice and water, will therefore be coexistent along the line  $OC$ , which shows a very considerable rise of pressure for a very slight fall of temperature. In this case also a change of pressure at a constant temperature, or the reverse, involves the complete disappearance of one of the phases. The line  $OC$  will end at a point where the liquid and solid phases become identical, i.e. where the whole system turns to a homogeneous amorphous mass. The location of this point has not yet been ascertained.

The point  $O$ , the melting-point of ice, is, according to the above mode of representation, the point of intersection of the three lines, which separate the phases and along which two phases are coexistent. It is called a **triple point**. Only in this point is it possible for the *three* phases to exist side by side; it is the common point of the areas which represent regions of the three phases. The more general significance which attaches itself to the melting-point as a result of the application of the phase rule is readily seen.

In the case of sulphur we have one substance and four possible phases: rhombic, monoclinic, liquid, gaseous. Fig. 33 makes plain the relation between these phases. Below  $95.4^\circ$  sulphur is rhombic; the two phases are rhombic sulphur and vapor. The line  $OA$  forms the boundary between the two regions. At  $95.4^\circ$  the rhombic phase passes into the monoclinic. The ordinates of the line  $OB$  represent the vapor pressure of monoclinic sulphur at the temperatures  $95.4^\circ$ – $120^\circ$ . The two crystallizable phases can exist side by side at the point  $O$  (the transition-point). According to researches by REICHER this transition point depends on the pressure; an increase of pressure of one atmosphere raises it about

0.05°. The boundary between the crystallized phases is therefore furnished by a line  $OC'$ , which shows that a very slight rise of temperature is followed by a very considerable increase of pressure. At  $O$  we have therefore a triple point, i.e. a point common to both crystallized and the gaseous phases. At  $B$ , the melting-point of monoclinic sulphur, there is a second triple point, which is wholly analogous to the melting-point of ice. Finally, it should also be noted that the line  $BC'$ , which separates the liquid and the solid phases, must indicate a rise of melting-point for an increase of pressure, since sulphur melts higher the greater the pressure. The lines  $OC'$  and  $BC'$  are not parallel but intersect, according to TAMMANN'S experiments, at 151° and 1281 atmospheres.

At the triple point neither the temperature nor the pressure can be changed without altering the kind of equilibrium. This is well expressed by saying that the system is **nonvariant**, or it has *no degree of freedom*. Along the lines  $OA$ ,  $OB$  and  $OC$ , however, any temperature may be selected and the pressure will under suitable conditions conform to it, or *vice versa*. This system is therefore **univariant**, or it has *one* degree of freedom. It is likewise easily seen that an unsaturated solution represents a **divariant** system, because in this case the temperature and pressure (within certain limits) can be selected at will.

We are now able to express the phase rule in a different way. There are in general  $n + 2$  phases when a system of  $n$  substances is nonvariant. If, then, we call the number of phases  $P$ , the number of substances  $B$  and the degrees of freedom  $F$ , we have in general:

$$P + F = B + 2,$$

every phase less giving one more degree of freedom.

#### HYDROGEN SULPHIDE, SULPHURETTED HYDROGEN, $H_2S$ .

72. This gas occurs in nature chiefly in volcanic regions. Certain mineral waters, especially the so-called "sulphur springs" contain it. It is also found as a putrefactive product of organic bodies.

Hydrogen sulphide can be obtained from its elements by synthesis. They unite almost completely when heated together for a long time (about 168 hours) at 310°.

It can also be obtained by the action of hydrogen on sulphur compounds as well as by the action of sulphur on compounds of hydrogen; the reduction of silver sulphide,  $\text{Ag}_2\text{S}$ , with hydrogen at high temperatures illustrates the former case, while the boiling of turpentine oil with sulphur is an example of the latter.

None of the above methods are adapted to the preparation of the gas in the laboratory. For this purpose the interaction of a sulphide with a hydrogen compound is employed, iron sulphide and dilute acids being generally used:



In order to have sulphuretted hydrogen always at hand, it being in constant demand in analytical work (*cf.* § 73), a very convenient apparatus was devised by KIPP, which can be used for the generation (at ordinary

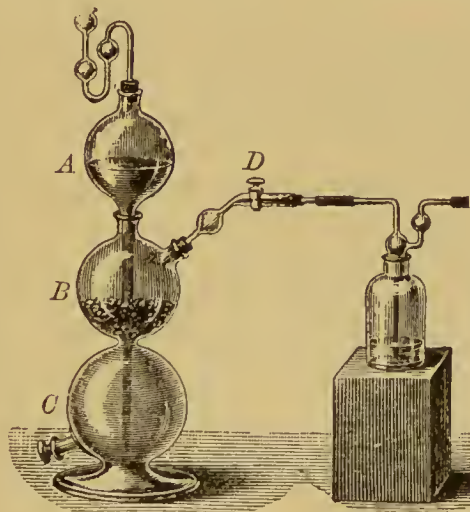


FIG. 34.—KIPP GENERATOR.

temperatures) of other gases as well. Its construction is shown in the figure.

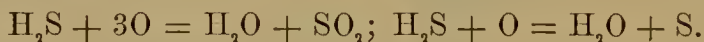
Two glass globes *B* and *C* are joined together by a narrow glass neck, while a long tube from a third globe *A* fits air-tight into an opening at the top of *B* and extends nearly to the bottom of the lowest globe without completely closing the passage from *B* to *C*. The iron sulphide is put in *B* and the dilute acid poured through *A* into *C*, the cock *D* remaining open. As soon as *C* is filled, the cock is closed, and *A* is then half-filled with more acid. When the cock is now opened the liquid sinks in *A* and rises into *B*, reacting with the iron sulphide to produce  $\text{H}_2\text{S}$ , which escapes through *D*. On closing the cock the gas continues to be evolved till it forces the liquid out of *B*; the reaction thus ceases automatically and the generator is

ready at any time to supply new quantities of gas on opening the cock, till either acid or sulphide is exhausted. The spent acid can be let out through a stoppered opening in *C*.

On account of the free iron usually present in iron sulphide, the gas prepared in this manner contains some hydrogen. Perfectly pure  $H_2S$  is obtained by warming antimony sulphide,  $Sb_2S_3$ , with concentrated hydrochloric acid.

*Physical Properties.*—Hydrogen sulphide is a colorless gas of disagreeable odor, when diluted reminding one of rotten eggs. Under a pressure of about 17 atmospheres it becomes liquid at ordinary temperatures; liquid hydrogen sulphide boils at  $-61.8^\circ$  and freezes at  $-85^\circ$ . The gas is rather soluble in water, 1 vol. water dissolving 4.37 vols.  $H_2S$  at  $0^\circ$  ("hydrogen sulphide water"). It is poisonous; as an antidote very dilute chlorine may be inhaled.

*Chemical Properties.*—Hydrogen sulphide is combustible and yields on combustion either sulphur dioxide and water or water and sulphur, according to the air-supply:



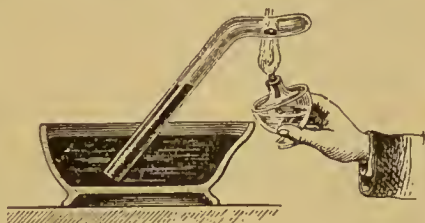
In aqueous solution it is slowly oxidized by the oxygen of the air, sulphur being set free; this decomposition is aided by light. In order to preserve sulphuretted hydrogen, it must be prepared from boiled (air-free) water and put into a dark bottle, filled entirely and closed air-tight. The latter condition is best met by placing the bottle, stopper downwards, in a glass of water.

Hydrogen sulphide is a powerful reducing agent. Bromine water and iodine solution are decolorized by it with separation of sulphur (§§ 45 and 48).

Various oxygen compounds are transformed by hydrogen sulphide into compounds with less oxygen, e.g. chromic acid is reduced in acid solution to a chromic salt (§ 295). Fuming nitric acid acts so vigorously that a slight explosion occurs. When hydrogen sulphide is passed over lead dioxide, it ignites, while the latter is reduced. Concentrated sulphuric acid,  $H_2SO_4$ , is also reduced; hence it cannot be used for drying the gas.

Hydrogen sulphide possesses the character of a weak acid; when it is passed over zinc, copper, tin or lead, the corresponding sulphides are formed and hydrogen is set free.

*Composition of hydrogen sulphide.* When a bit of tin is heated in dry hydrogen sulphide—in a tube over mercury,—tin sulphide and hydrogen are formed. After cooling it is seen that the volume of hydrogen is just as great as that of the hydrogen sulphide. The same result is obtained when a platinum wire is heated to redness (by an electric current) in the dry gas, causing the latter to break up into its elements. Since the hydrogen molecule is  $H_2$ , there must be two atoms of hydrogen in the hydrogen sulphide molecule. Now the specific gravity of hydrogen sulphide has been found to be 1.1912 for air = 1, or 17.15 for  $O = 16$ . The grammolecule therefore weighs 34.30 g., and, as it contains 2 g. hydrogen, there remains for sulphur 32.3 g. This figure is very close to the atomic weight of sulphur, hence there can only be one atom of sulphur present in the molecule of hydrogen sulphide. We thus conclude that the formula is  $H_2S$ .

FIG. 35.—DECOMPOSITION OF  $H_2S$ .

**73. Use of Hydrogen Sulphide in Analysis.**—Hydrogen sulphide finds extensive use in qualitative analysis. A large number of metals are precipitated by it from acid solutions as sulphides. These are, with the exception of certain rare elements, gold, platinum, arsenic, antimony, tin, silver, mercury, lead, bismuth, copper and cadmium. Some of these sulphides have a characteristic color, e.g. the orange-red antimony sulphide,  $Sb_2S_3$ , the yellow cadmium sulphide,  $CdS$ , the brown stannous sulphide,  $SnS$ , the yellow stannic sulphide,  $SnS_2$ , and the yellow arsenic sulphide,  $As_2S_3$ . The rest of the sulphides named are black. Other metals, such as nickel, cobalt, iron, manganese, zinc, chromium, aluminium, etc., are not precipitated by hydrogen sulphide from acid solution, but are precipitated by ammonium sulphide. Still other metals, such as barium, strontium, calcium, magnesium and the alkalis, are not precipitated from their solutions even by ammonium sulphide, so that we therefore possess in sulphuretted hydrogen and its ammonium compound a means of separating these elements.

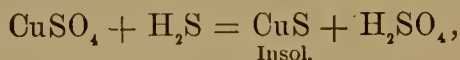
An answer to the question, why some elements are precipitated from acid solution by hydrogen sulphide and others not, is furnished by the ionic theory. Given, for example, a dilute solution

of copper sulphate, into which hydrogen sulphide is being passed. Copper sulphate is almost entirely ionized, hydrogen sulphide only in a very small amount ( $\delta$ ). We therefore have in the solution

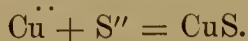


the cations being represented by a point and the anions by a line above and to the right, and the number of these points or lines indicating their valence (§ 76).

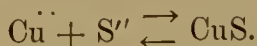
The copper ions and sulphur ions will then unite partially to form undissociated molecules,  $\text{CuS}$ , which are only slightly soluble in water and are therefore precipitated. As S-ions thus disappear, the equilibrium between hydrogen sulphide and its ions is disturbed; new  $\text{H}_2\text{S}$  molecules are then split up into ions, so that there are again S-ions present, which can unite with copper and so on. The action proceeds according to the equation:



or, if only the ions which take part in it are represented:



This takes place quantitatively if the copper solution is dilute and no considerable amount of any strong free acid was added. However, if these conditions are not fulfilled and if the concentration of the hydrogen ions is therefore rather great, the latter reduce the ionization of  $\text{H}_2\text{S}$  so much (§ 66) that no precipitate can be formed. The formation of this precipitate depends namely on the following condition: Copper sulphide, when in contact with water, dissolves to an extremely small extent; in this solution we have the equilibrium



If the concentrations of the two ions are  $a$  and  $b$ , and that of the undissociated copper sulphide is  $c$ , we have the equation

$$ab = k \cdot c,$$

$k$  being a constant for a fixed temperature (§ 66).

The product  $ab$  is known as the **solubility product**. For every saturated solution it has a definite value. If in any given case it

be less than this value, nothing can separate out from the solution, because the solution will then be unsaturated; if, however, it be greater for some reason or other, the dissolved substance is precipitated.

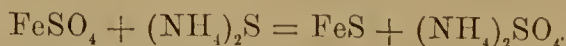
As soon then as the concentration of the S-ions becomes so small (because of the reduction of the ionization of hydrogen sulphide by the H-ions of the acid) that it makes the value of  $ab$  smaller than that of the solubility product for copper sulphide, no precipitate will be formed. If, however, the liquid is diluted, the concentration of the H-ions decreases; then, if hydrogen sulphide is passed in, that of the S-ions increases. The value of the solubility product can in this way be exceeded, in which event copper sulphide will be precipitated.

If a strong acid be added to a precipitate of copper sulphide suspended in water, only a very small amount of the latter will dissolve; to be sure, the H-ions of the strong acid will remove a part of the S-ions, yielding some undissociated hydrogen sulphide, so that in order to establish equilibrium a trace of copper sulphide must go into solution; but soon the point will be reached when so many Cu- and S-ions are again in the solution that the value of the solubility product is reached. After this moment no more copper sulphide goes into solution. Since the value of the solubility product is very low, the solubility of the sulphide in dilute strong acids is very slight; hence the precipitation of the copper sulphide becomes possible.

On the other hand, if the solubility product of a sulphide is greater, as in the case of iron sulphide, the addition of sulphuretted hydrogen to the solution of an iron salt, e.g. ferrous sulphate,  $\text{FeSO}_4$ , will cause no precipitate of iron sulphide, and iron sulphide will, unlike the previous case, be dissolved by dilute strong acids. When hydrogen sulphide is led into a solution of ferrous sulphate to the point of saturation, the concentration of the S-ions is, on account of the slight ionization of hydrogen sulphide, not great enough together with that of the Fe-ions to reach the solubility product of iron sulphide, hence no precipitate forms. Moreover, when dilute hydrochloric acid is added to iron sulphide, the H-ions and the S-ions form undissociated  $\text{H}_2\text{S}$  molecules and the concentration of the S-ions does not therefore become great enough in comparison with the value of the solubility product to

prevent solution; hence in the presence of enough acid all the iron sulphide goes into solution.

It now becomes clear, too, why iron solutions are precipitated by ammonium sulphide. This takes place according to the equation



In this case there are no H-ions in the solution to act on the iron sulphide.

The reason for the non-precipitation of metals like barium, etc., either by sulphuretted hydrogen or ammonium sulphide lies in the easy solubility of their sulphides.

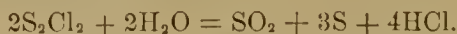
#### Hydrogen Persulphide.

74. On boiling a solution of a base, potash or lime, with sulphur, polysulphides are formed, i.e. compounds like  $\text{K}_2\text{S}_2$ ,  $\text{K}_2\text{S}_3$ , etc., up to  $\text{K}_2\text{S}_6$  or  $\text{CaS}_6$ . When a solution of these substances is treated with hydrochloric acid, a dense oily liquid, hydrogen persulphide, separates out, whose composition is approximately represented by the formula  $\text{H}_2\text{S}_6$ . It is, however, very unstable; it can not, for instance, be distilled, even in a vacuum.

#### Compounds of Sulphur with the Halogens.

75. If chlorine is conducted over molten sulphur, sulphur monochloride,  $\text{S}_2\text{Cl}_2$ , is formed. Its formula is based on its vapor-density and analysis. It is a yellow liquid of a very disagreeable, pungent odor, which excites one to tears. It boils at  $139^\circ$  and possesses in a high degree the ability to dissolve sulphur—at ordinary temperatures as much as 66%. This solution is a thick syrupy liquid. It is used in the vulcanizing of rubber.

It is slowly decomposed by water.



Sulphur dichloride,  $\text{SCL}_2$ , is obtained when the monochloride is saturated with chlorine at a temperature of  $6^\circ$ – $10^\circ$  and the excess of chlorine then expelled by a current of carbonic acid. It is a dark red liquid and is also decomposed by water.

Sulphur tetrachloride,  $\text{SCL}_4$ , is formed when the monochloride is saturated with chlorine at  $-22^\circ$ . It is stable only at temperatures as low as this; at  $0^\circ$  it is chiefly dissociated into  $\text{Cl}_2$  and  $\text{SCL}_2$ ; at  $+6^\circ$  this dissociation is complete, the vapor-density being then reduced one-half, as the separation of  $\text{SCL}_4$  into  $\text{SCL}_2$  and  $\text{Cl}_2$  requires. Sulphur tetrachloride forms crystallized



compounds with certain other chlorides, thus  $2\text{AlCl}_3 \cdot \text{SCl}_4$ ,  $\text{SnCl}_4 \cdot 2\text{SCl}_4$ , etc. It is a yellowish-brown, very mobile liquid.

The existence of the compounds  $\text{SCl}_2$  and  $\text{SCl}_4$  in the free state is by no means so definitely established as one would conclude from the statements in almost all text-books. However, one argument that was formerly urged against their existence has been shown by the phase rule to be of no consequence, viz., the fact that the tension of a solution of chlorine in the monochloride at a constant temperature depends on the amount of chlorine contained. It was thought that this tension must be independent of it up to a definite point, when  $\text{S}_2\text{Cl}_2$  or  $\text{SCl}_4$  should be formed, for then we should have a mixture of  $\text{S}_2\text{Cl}_2$ ,  $\text{SCl}_2$  and  $\text{SCl}_4$ , whose partial tensions together would produce the total tension. So long as these three substances are present—it was assumed—the tension of the solution at a given temperature must remain constant. However, we have here according to GIBBS (§ 71) two substances (sulphur monochloride and chlorine) and only two phases (the solution and the gas), hence an incomplete heterogeneous equilibrium, in which case the vapor tension at constant temperature is a variable. We can conceive this also in the following way: the tension of a mixture of liquids depends on their relative quantities, because their mutual presence diminishes the vapor pressure of each, and this diminution is a function of their quantities.

**Bromine** and **iodine** yield sulphur compounds analogous to those of chlorine. Sulphur introduced into **fluorine** burns and gives a compound  $\text{SF}_6$ , a gas which is not decomposed at ordinary temperatures by water, alkalis or quicksilver; at  $-55^\circ$  it becomes a white crystalline mass.

## VALENCE.

**76.** Certain elements have the property whereby their atoms can combine with only one atom of another element. The halogens on the one hand and hydrogen on the other are able to form only compounds of the type  $\text{HX}$  ( $\text{X} =$  halogen). This property of the atoms is called **univalence**.

In the case of other elements like oxygen and sulphur each atom can enter into compounds with two univalent atoms (examples:  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$ ). These are therefore called **bivalent**.

The number of univalent atoms that can combine with one atom of a given element serves in an analogous way as a measure of valence in general. An atom of nitrogen, for instance, unites with three atoms of hydrogen; nitrogen is therefore trivalent; carbon is quadrivalent, etc.

The valence of one and the same element may be different

according to the nature of the univalent elements with which it combines. Sulphur, for instance, can only unite with two hydrogen atoms, but with univalent chlorine it forms the compound  $\text{SCl}_4$ , with fluorine even  $\text{SF}_6$ . The valence of sulphur in these cases is therefore four and six. The preparation of sulphur compounds with *more* than six univalent atoms has not yet been accomplished; hence its **maximum valence** is six.

The halogens are univalent towards hydrogen, but in relation to each other they are plurivalent, as may be seen from the compounds  $\text{ICl}_3$  and  $\text{ICl}_5$ ; in the compound  $\text{Cl}_2\text{O}_7$  (§ 60) the maximum valence of chlorine can even be assumed to be seven.

It has been quite generally observed that when the maximum valence of an element is an even or an uneven number, its lower valences are of the same sort; the halogens and sulphur illustrate this. However, there are exceptions to this rule.

The number of *bivalent* atoms which combine with an atom of another element can also serve as a measure of valence. We shall soon become acquainted with compounds of sulphur,  $\text{SO}_2$  and  $\text{SO}_3$ , in which its valence may be considered as four and six; this is made clear by the formulæ

$\text{S} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$  and  $\text{S} \begin{array}{c} \diagup \text{O} \\ \text{O} \\ \diagdown \text{O} \end{array}$ , in which each line stands for a valence (unit bond). It

should, however, be noted that sulphur may also be considered as bivalent in these compounds, according to the formula  $\text{S} < \begin{array}{c} \text{O} \\ \text{O} \end{array}$ . This differs from

the above only by the assumption of a bond between the oxygen atoms. Which of the two formulæ for  $\text{SO}_2$  is correct has not yet been determined.

The basis for this sort of formulæ is the idea, borrowed from organic chemistry, that the atoms of a molecule may not assume any conceivable arrangement whatsoever, but that there is a definite order in every molecule.

**Valence of Ions.**—In the solution of an electrolyte the sums of all the positive and all the negative amounts of electricity must be equal, for the solution acts as electrically neutral. In a solution of hydrochloric acid the positive charge of the H-ions must be numerically equal to the negative charge of the Cl-ions and, since the same number of both ions are present, every one of them must carry the same but opposite charge. In a sulphuric acid solution, however, the two H-ions together must possess just as much positive electricity as the  $\text{SO}_4$ -ion negative electricity. The  $\text{SO}_4$ -ion is therefore called bivalent in respect to the hydrogen ion. It is readily

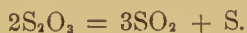
seen how the valence of other ions can be determined in an analogous manner; it is indicated by the numerical value of their electrical charge, that of the hydrogen atom being taken as unity.

### Compounds of Sulphur with Oxygen.

77. Of those containing only the two elements four are known, viz.,  $S_2O_3$ ,  $SO_2$ ,  $SO_3$  and  $S_2O_7$ . Especial importance attaches itself, however, only to  $SO_2$  and  $SO_3$ ; the two others have been little studied.

#### Sulphur Sesquioxide, $S_2O_3$ .

This is obtained when sulphur is treated with the trioxide. It is a blue liquid, which congeals to a malachite-green mass and is soluble in fuming sulphuric acid, giving a blue solution. On being warmed it breaks up into sulphur and the dioxide:



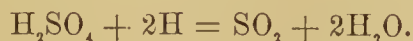
Water decomposes it with the formation of sulphur, sulphurous acid and polythionic acids.

#### SULPHUR DIOXIDE, SULPHUROUS ANHYDRIDE, $SO_2$ .

78. This gas occurs in nature in volcanic gases. It is formed when sulphur burns in the air or in oxygen; the well-known odor of burning sulphur is due to it. A little trioxide is also formed by this combustion. The laboratory method of preparation consists in decomposing sulphuric acid with copper.



For this purpose concentrated sulphuric acid is heated with copper turnings, no action taking place at ordinary temperatures. The process can be explained by supposing that at the high temperature of the reaction copper first displaces the hydrogen from a molecule of acid; the hydrogen then reacts with a second molecule of acid, reducing it thus:



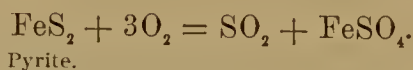
It has actually been found that concentrated sulphuric acid is reduced at a high temperature to sulphurous oxide by leading in hydrogen.

The reduction of concentrated sulphuric acid by heating with charcoal is also a convenient method of preparation:



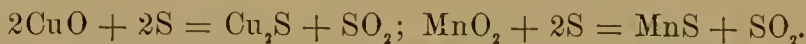
However, as this equation shows, the gas is obtained mixed with one third of its volume of carbon dioxide, from which it cannot be separated directly.

Moreover, sulphur dioxide can be obtained by the action of oxygen on sulphur compounds, thus, e.g. by the roasting of pyrite in a current of air:

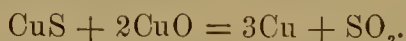


This reaction is employed on a large scale in the commercial manufacture of sulphuric acid.

The action of sulphur on oxygen compounds also yields sulphurous oxide, e.g. heating copper oxide or manganese dioxide with sulphur:



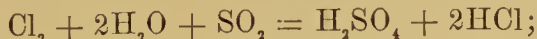
Finally, the dioxide is formed by heating an oxygen compound (CuO) with a sulphur compound (CuS):



*Physical Properties.*—At ordinary temperatures and pressures sulphur dioxide is a gas. It has a peculiar taste and odor. It is easily liquefied, the boiling-point being  $-8^\circ$ . Its evaporation produces a marked depression of temperature, sometimes extending to  $-50^\circ$ ; at  $-76^\circ$  it becomes solid. Liquid sulphur dioxide dissolves many salts, in some cases with a characteristic color. It is very soluble in water; at  $0^\circ$  1 vol.  $\text{H}_2\text{O}$  dissolves 79.79 vols.  $\text{SO}_2$ ; at  $20^\circ$  39.37 vols.  $\text{SO}_2$ . Boiling the solution expels all the gas (§ 84).

*Chemical Properties.*—Sulphur dioxide is an acid anhydride. its aqueous solution has a sour reaction and behaves in general like that of an acid (§ 84). It is easily oxidized by oxidizing agents to the trioxide. This occurs, for instance, when a mixture of sulphur dioxide and air or oxygen are passed together over hot spongy platinum or platinum asbestos. In aqueous solution this oxidation

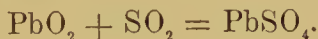
takes place readily at ordinary temperatures. The oxidation of the dioxide can also be brought about by chlorine water, bromine and iodine:



also by chromic acid, which is reduced to chromium sulphate, or by potassium permanganate, which is reduced to a mixture of manganese and potassium sulphates and therefore loses its color:



Lead peroxide starts to glow in a current of sulphur dioxide and is reduced to lead sulphate—from brown to white:



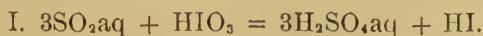
It is to its reducing action that the bleaching effect of sulphurous oxide on vegetable coloring-matters is due. A red rose, for example, loses color in it. The gas probably reacts with water, setting hydrogen free, which latter effects the reduction and hence the bleaching:



In this case therefore bleaching depends on a reduction; as a matter of fact the color returns in many cases, when the bleached article is exposed to the oxidizing action of the air. Silk, woolen and straw, i.e. substances that cannot stand the chlorine bleaching, are whitened commercially with sulphurous oxide. It also finds use as an antiseptic.

The reduction of iodic acid by sulphur dioxide is sometimes employed as a test for the latter. For this purpose strips of paper are dipped in a solution of potassium iodate and starch, which turns blue in the presence of sulphur dioxide—iodine being set free (§47.)

If the reaction is carried out in dilute solution, a peculiar phenomenon is observed; the blue color of starch iodide does not appear directly when the solutions of  $\text{SO}_2$  and  $\text{HIO}_3$  are mixed, but is withheld for a certain number of seconds (definite for every concentration at constant temperature), when it suddenly appears. The following reactions come into play:



The hydriodic acid thus formed is at once oxidized by the iodic acid still present:



So long as  $\text{SO}_2$  is present, it reduces the iodine in this dilute solution to HI:



Not until all the dioxide is used up by the reactions I and III does the free iodine suddenly appear according to II.

There are some substances which are able to extract oxygen from sulphur dioxide, i.e. the latter can also act as an *oxidizing agent*. Ignited magnesium ribbon continues to burn in sulphur dioxide, forming magnesium oxide and sulphur. Hydrogen sulphide and sulphur dioxide have respectively an oxidizing and a reducing effect on each other which follows mainly the equation:



It is decomposed by electric sparks into sulphur and the trioxide.

The action of the electric sparks is to be ascribed solely to the sudden and enormous rise of temperature which they produce and the rapid cooling that immediately follows, for the gas particles which have become heated by the sparks are immediately cooled again by surrounding objects. As a result the products formed do not have time to react in the opposite direction. The correctness of this view was demonstrated by ST. CLAIRE DEVILLE with the help of an apparatus which made it possible to cool objects very rapidly from a very high temperature. This apparatus, the cold-hot tube, consists of a rather wide porcelain tube, which is heated to a bright glow in a furnace and which contains a concentric thinner metallic tube, through which cold water is forced so rapidly that the tube maintains a low temperature. When DEVILLE introduced sulphur dioxide into the space between the two tubes, it was seen after some time that the inner tube, which was made of silver-plated copper, had turned black because of the formation of silver sulphide, while at the same time the formation of sulphur trioxide could be detected (by its producing sulphuric acid with water, a precipitate being given by barium chloride).

The *composition* of sulphur dioxide can be determined in the following manner: When sulphur burns in oxygen no change of volume is observed after cooling. Therefore just as many molecules of sulphurous oxide have been formed as oxygen molecules consumed. The sulphur dioxide molecule must therefore contain two atoms of oxygen. The specific gravity of the gas has been found to be 2.2639 (air = 1), or 32.6 (O = 16), so that its molecular weight is 65.2. If we subtract  $2 \times 16$  from this for two

atoms of oxygen, there remains 33.2 for sulphur, the atomic weight of which is 32. We thus see that only one atom of sulphur is present in the molecule of sulphurous oxide and that the formula of the latter is  $\text{SO}_2$ .

#### SULPHUR TRIOXIDE, SULPHURIC ANHYDRIDE, $\text{SO}_3$ .

79. This compound is found in a small amount in the fumes of burning sulphur (§ 78). As was stated above, oxygen and sulphur dioxide unite to form the trioxide in the presence of platinized asbestos. A similar contact action is also brought about by iron oxide,  $\text{Fe}_2\text{O}_3$ , chromium oxide,  $\text{Cr}_2\text{O}_3$ , and a few other substances. Upon this is based a commercial process for the manufacture of sulphur trioxide (see § 86). The catalytic action of those substances must be regarded as in the previous cases (§ 49), that is, the combination of  $\text{SO}_2$  and O takes place also without the catalyzer, but very slowly. The formation of a small amount of  $\text{SO}_3$  on burning sulphur proves it. The action of the catalyzer only consists in accelerating the process.

Sulphur trioxide can also be obtained by heating certain sulphates; in the arts ferric sulphate is thus used:



“Fuming sulphuric acid” (oleum) is a solution of sulphur trioxide in sulphuric acid; the anhydride can be obtained from it by distillation.

*Physical Properties.*—Sulphur trioxide is at ordinary temperatures a thin mobile liquid (boiling-point  $46^\circ$ ), which can be cooled to  $0^\circ$  without solidifying, but on being cooled still more forms an ice-like mass, melting at  $15^\circ$ . It is best known in another modification, viz., as long needle-like crystals having a silken lustre and the general appearance of asbestos. These crystals do not melt, but on heating them they turn directly to vapor. This modification is the stable one; the other changes spontaneously into this one, and is thus the unstable modification. It is probable that the asbestic form consists of  $(\text{SO}_3)_n$  molecules, in which  $n$  is still undetermined, while the glacial form consists of  $\text{SO}_3$  molecules. The first would thus be a *polymer* of the latter.

*Chemical Properties.*—Sulphur trioxide unites very easily with water to form sulphuric acid:



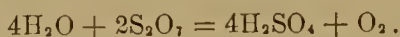
It therefore fumes vigorously when exposed to moist air. On introducing it into water, combination and great evolution of heat, accompanied by sizzling, results. It reacts energetically with many metallic oxides also, forming sulphates. Baryta, for example, glows in contact with it. When its vapor is passed through a red-hot tube, it is decomposed into dioxide and oxygen.

*Composition.*—The decomposition just mentioned permits us to establish the composition of sulphuric oxide. The dissociation products,  $\text{SO}_2$  and  $\text{O}_2$ , are formed in the volume ratio 2 : 1. Now the vapor density of sulphuric oxide is 2.75 (air = 1), from which the molecular weight is calculated to be 79.1. This figure corresponds to the formula  $\text{SO}_3$  ( $32 + 3 \times 16$ ) and it also harmonizes with the above dissociation; for it is clear that 2 vols.  $\text{SO}_3$  must then yield 2 vols.  $\text{SO}_2$  and 1 vol.  $\text{O}_2$ :



#### Sulphur Heptoxide, $\text{S}_2\text{O}_7$ .

80. This compound is formed when a mixture of equal volumes of dry oxygen and sulphur dioxide is subjected to a dark electric discharge of high potential. It consists of oily drops which crystallize below  $0^\circ$  and slightly above that temperature break up into trioxide and oxygen. With water it forms sulphuric acid and oxygen:



#### Oxygen Acids of Sulphur.

81. Sulphur forms an unusually large number of acids with oxygen and hydrogen, namely nine. They are as follows:

1. Thiosulphuric acid. . . . .  $\text{H}_2\text{S}_2\text{O}_3$ .
2. Hyposulphurous acid . . . . .  $\text{H}_2\text{S}_2\text{O}_4$ .
3. Sulphurous acid. . . . .  $\text{H}_2\text{SO}_3$ .
4. Sulphuric acid. . . . .  $\text{H}_2\text{SO}_4$ .
5. Persulphuric acid . . . . .  $\text{H}_2\text{S}_2\text{O}_8$ .
6. Dithionic acid. . . . .  $\text{H}_2\text{S}_2\text{O}_6$ .
7. Trithionic acid. . . . .  $\text{H}_2\text{S}_3\text{O}_6$ .
8. Tetrathionic acid. . . . .  $\text{H}_2\text{S}_4\text{O}_6$ .
9. Pentathionic acid . . . . .  $\text{H}_2\text{S}_5\text{O}_6$ .



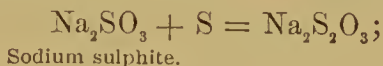
It is an important fact, however, that of these nine acids only sulphuric acid has really been isolated ; all the others are known only in aqueous solution or in the form of salts. The two hydrogen atoms which each of these acids possesses are both replaceable by metals ; they are therefore *dibasic* acids. With such acids it is possible that just one of the hydrogen atoms be replaced by a metal. The salts thus formed are called **acid salts**.

By different methods, for instance the cryoscopic, it is found, that the aqueous solution of dibasic acids  $AH_2$  contains chiefly the ions  $\overset{+}{H}$  and  $HA'$ ; it is only when these solutions are very dilute that the anion  $HA'$  itself splits up into  $\overset{+}{H}$  and  $A''$ . In the case of the  $M_2A$  salts, however, there is an ionization into  $2\overset{+}{M} + A''$ ; but in that of the acid salts  $MHA$  the ions are chiefly  $\overset{+}{M}$  and  $HA'$ . How far the anion  $HA'$  is split up does not depend merely on the concentration, but also in a considerable degree on the strength of the acid,  $HA'$  being more ionized in strong than in weak acids of the same concentration.

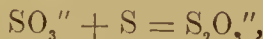
**THIOSULPHURIC ACID,  $H_2S_2O_3$ .**

82. This acid can only exist in dilute aqueous solution and is even then very unstable, decomposing completely in a short time. The salts are, however, stable and can be prepared in the following ways:

1. By boiling the solution of a sulphite with sulphur:

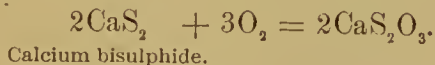


or



only the anion being changed.

2. By the oxidation of sulphides in the air:



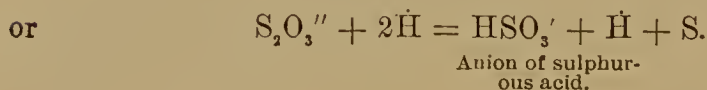
3. By the action of sulphur dioxide on the solution of a sulphide:



The most important salt is the sodium thiosulphate, formerly and even yet often called sodium hyposulphite, or abbreviated "hypo". It is very soluble in water; the solution, when used in excess, has the property of dissolving readily the halogen compounds of silver, hence its extensive use in photography (§ 247).

It is easily oxidized by oxidizing agents, usually to the sulphate. This takes place with potassium permanganate, nitric acid and chlorine, for example. Practical use is also made of this latter property by employing sodium thiosulphate as an *antichlor* in bleaching, i.e. to remove the last traces of chlorine which cling to the bleached material very obstinately and have an injurious effect.

When a dilute acid is added to a dilute solution of sodium thiosulphate, the following decomposition takes place:



It may be, however, that the ions first unite partially to form  $\text{H}_2\text{S}_2\text{O}_3$ , which splits up into  $\text{H}_2\text{O}$ ,  $\text{S}$  and  $\text{SO}_2$ .

It is an interesting fact that in this decomposition in a dilute solution the sulphur precipitate is not at once visible, being first noticeable after some seconds, or even minutes according to the dilution. It was formerly supposed that the thiosulphuric acid remained entirely unchanged until the appearance of the sulphur and the decomposition first began at this moment. This is, however, incorrect; for when a dilute solution of thiosulphate is treated with an equivalent amount of dilute acid and the solution again neutralized before the appearance of the sulphur deposit, it is found that the latter appears nevertheless after some time. A certain part of the free thiosulphuric acid must therefore have already decomposed, but the sulphur was in a so very finely divided state in the liquid that it could not at once be detected,—not until it had gathered together to form larger particles.

#### Hyposulphurous Acid, $\text{H}_2\text{S}_2\text{O}_4$ .

83. As early as the 18th century it was observed that zinc is dissolved by a solution of sulphur dioxide in water without the evolution of hydrogen. SCHÜTZENBERGER was, however, the first to show that a particular acid is formed thereby. A salt of this acid is produced by the action of zinc on a solution of acid sodium sulphite,  $\text{NaHSO}_3$ , or by the electrolysis of such a solution, the nascent hydrogen acting as a reducing agent.

Hyposulphurous acid, as well as its salts, is characterized by a vigorous reducing power. It precipitates the metals from solutions of sublimate ( $\text{HgCl}_2$ ), silver nitrate and copper sulphate. Iodine solution is bleached by it with the formation of hydrogen iodide; indigo is reduced to indigo-white. The solution is also very easily oxidized by free oxygen. It is

therefore used to determine the amount of oxygen dissolved in water. For this reason it must be kept in well-stoppered vessels.

BERNTHSEN has recently succeeded in preparing the solid sodium salt, which proved to have the composition  $\text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O}$ , so that the acid itself has the formula  $\text{H}_2\text{S}_2\text{O}_4$ .

This salt was obtained in preparing a concentrated solution of it, from which it could be separated by the addition of a suitable amount of solid common salt.

#### SULPHUROUS ACID, $\text{H}_2\text{SO}_3$ .

84. It is taken for granted that the aqueous solution of sulphur dioxide contains sulphurous acid,  $\text{H}_2\text{SO}_3$ , for this solution reacts acid, conducts the electric current, gives salts with bases and evolves hydrogen with some metals, e.g. magnesium. The solution of sulphur dioxide in water does not conform to the law of HENRY (§ 9) at ordinary temperatures, which proves that a combination with the solvent has taken place. At higher temperatures, however, the solution obeys this law pretty well. A fact in confirmation of this is, that all the sulphur dioxide can be expelled from the solution by boiling it, the combination being then wholly destroyed. The compound  $\text{H}_2\text{SO}_3$  itself has, however, not yet been isolated. The salts have the composition  $\text{M}_2\text{SO}_3$  and  $\text{MHSO}_3$  (M being an atom of a univalent metal). The acid salts are almost all soluble in water, while of the neutral salts only those of the alkalies are soluble. The acid sodium sulphite,  $\text{NaHSO}_3$  (sodium bisulphite), is frequently employed in organic chemistry. Sulphites in solution gradually absorb oxygen from the air, forming sulphates. It is a very strange fact that minute quantities of organic substances, e.g. only 0.1% of alcohol, greatly hinder this oxidation. We have here an example of a retarding catalytical action.

#### SULPHURIC ACID, $\text{H}_2\text{SO}_4$ .

85. Sulphuric acid is the most important acid of sulphur. It can be obtained in various ways; in the first place by direct synthesis from its elements. According to § 79 sulphur trioxide can be formed directly from sulphur and oxygen, and this yields sulphuric acid on the addition of water.

The acid can be obtained from its salts by distilling them with phosphoric acid. Its formation from the action of oxygen on sulphur compounds is illustrated by the oxidation of an aqueous  $\text{SO}_2$ -solution by the air. On the other hand the action of sulphur

on oxygen compounds may also give sulphuric acid; thus it is formed when concentrated nitric acid,  $\text{HNO}_3$ , is boiled with sulphur; and again, potassium sulphate is formed by heating sulphur with saltpetre ( $\text{KNO}_3$ ).

86. For the *commercial manufacture* of sulphuric acid two processes are now in use, the lead-chamber process and the contact process. Enormous amounts of the acid are produced by these two methods.

The lead-chamber process is based on the following reactions: 1. the oxidation of sulphur dioxide by nitric acid in the presence of water; 2. the oxidation by the oxygen in the air of lower oxides of nitrogen formed from the nitric acid in the previous reaction. These are partly reconverted to nitric acid and partly changed to certain stages of oxidation of nitrogen which oxidize sulphur dioxide anew to sulphuric acid. By this last process the lower nitrogen oxides are again formed, but are soon reoxidized by atmospheric oxygen and so on. One might suppose that a certain amount of nitric acid would suffice to convert unlimited amounts of sulphur dioxide into sulphuric acid with the aid of the air. In practice this is not true, however; for the nitrogen oxides are to a small extent still farther reduced by sulphurous oxide, so that nitrous oxide or nitrogen are formed, and these are no longer able, under the conditions of the industrial process, to combine with oxygen.

As may be seen from the above, the chemical process which lies at the basis of the manufacture of sulphuric acid is a very complicated one. As a matter of fact it has not yet been possible to explain it fully. In the main it takes the following course:

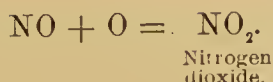
I. Sulphur dioxide is oxidized to sulphuric acid by nitric acid in the presence of water:



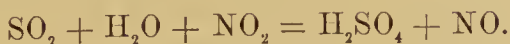
The nitric oxide (NO) thus formed is again oxidized by oxygen and water to nitric acid:



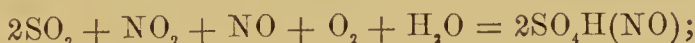
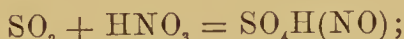
II. However, the nitric oxide may absorb oxygen according to a still different reaction:



This nitrogen dioxide also has the ability to oxidize sulphurous oxide with the re-formation of nitric oxide:



III. Sulphurous oxide and nitric acid, or sulphurous oxide, nitrogen dioxide, oxygen and water, can react with each other so that a crystallized compound, nitrosyl sulphuric acid,  $\text{SO}_2\text{OH}(\text{ONO})$  ("lead-chamber crystals"), are formed. These are decomposed by water into  $\text{NO} + \text{NO}_2$  and sulphuric acid:



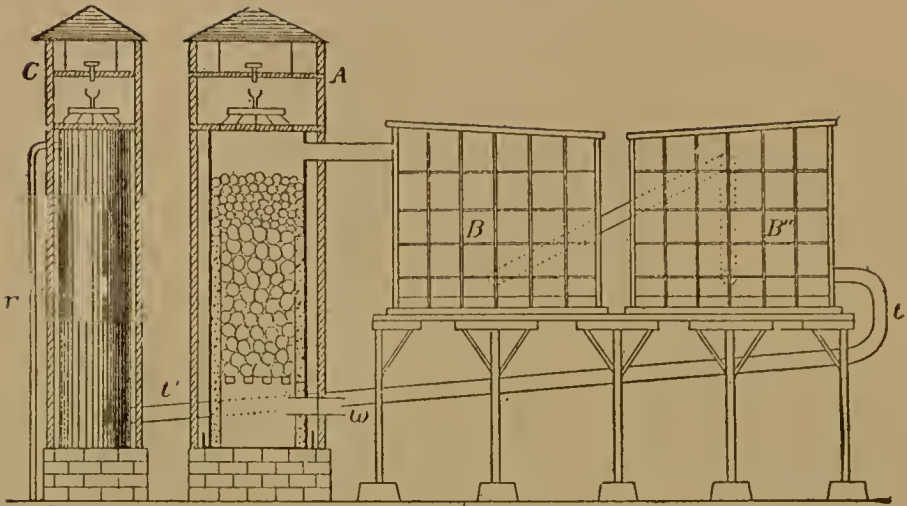
From a technical standpoint the lead-chamber process falls into three separate parts:

1. The preparation of sulphur dioxide;
2. The oxidation of sulphur dioxide;
3. The concentration of the resulting acid.

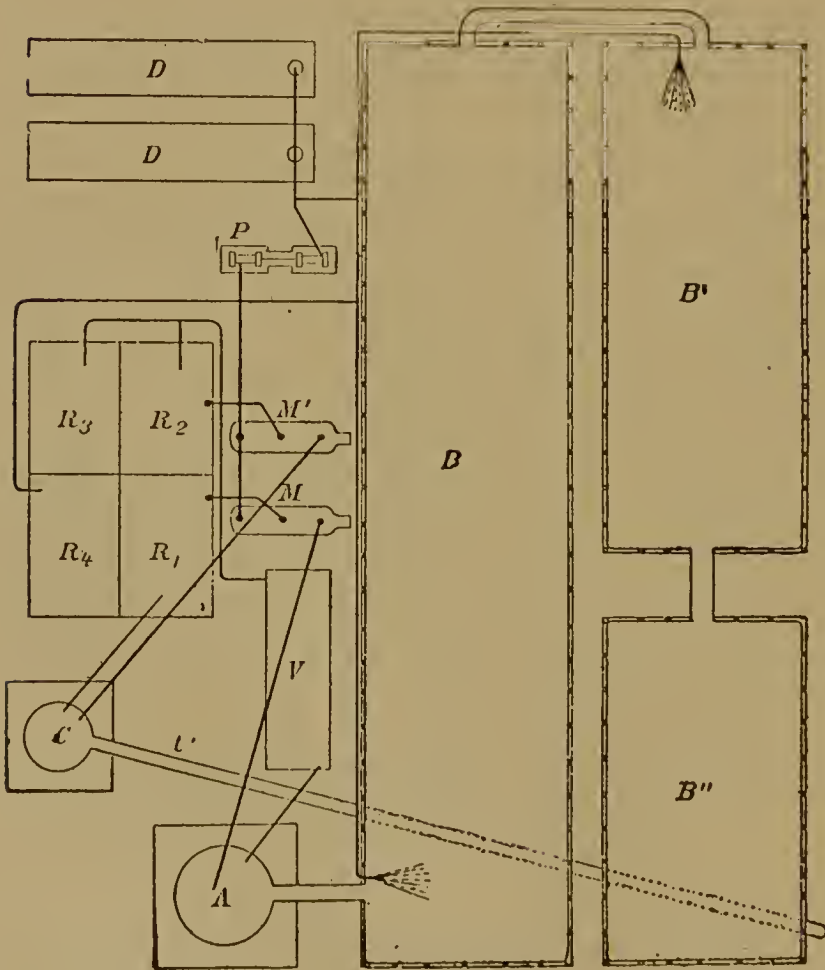
(1) The material for the production of the dioxide is sulphur or pyrite (iron pyrites,  $\text{FeS}_2$ ). Sulphur yields a purer acid than pyrite; that prepared from the latter almost always contains arsenic. The roasting of the pyrite is carried on in furnaces, the construction of which varies considerably. In all of them, however, the sulphur dioxide leaves the furnace mixed with a good deal of air. The furnace gases pass through a canal in which the dust particles carried along by the draught are deposited.

(2) The oxidation of the sulphurous acid is carried out in a structure (Fig. 37) consisting chiefly of three parts, the Glover tower, *A*, the lead-chambers, *B*, *B'*, *B''*, and the Gay Lussac tower, *C*.

The **Glover tower** is made of sheet lead lined with acid-proof brick. It is filled with lump stone over which is laid a layer of smaller pieces of coke. On top of the tower is a reservoir for col-



Elevation.



The terms :  
 B, B', B'', Lead chambers.  
 C, Gay Lussac tower.  
 A, Glover tower.  
 D, Water-boiler  
 r, Pipe to chimney.  
 t', Pipe from third chamber to the Gay Lussac.

Ground-plan.

FIG. 37 —SULPHURIC ACID FACTORY.

lecting the nitroso sulphuric acid (see p. 134) that comes from the Gay Lussac tower and the lead-chambers and is to be concentrated in the Glover tower. It flows down over the stone in the tower from a horizontally revolving tube.

The **lead-chambers** are three or four in number and have a total capacity of 4000–5000 cubic meters. Their form is that of a parallelepiped, whose cross-section is nearly a square. The length is either the same in all or it gradually increases from the first to the last. Lead has been chosen as the material for the walls of the chambers, because it is the only one of the common metals which is only slightly attacked by sulphuric acid and the substances used in its manufacture.

The lead-chambers are connected with each other, with the Glover tower and with the Gay Lussac tower by means of lead tubes so attached that the gases have to enter the upper part of the chamber and depart at the bottom, or *vice versa*. In the first two chambers, preferably near the tubes which supply the gases, but in other places as well, tubes are also introduced to conduct steam from the boilers, *DD*.

The walls of the **Gay Lussac tower** are likewise of lead. Here, however, it does not have to be protected by fire-brick, since the temperature of the gases coursing through the tower is not so high. Usually it is entirely filled with coke. On top of the tower is a reservoir containing 60°–62° sulphuric acid (BAUMÉ, see p. 140), which comes from the Glover tower.

Let us now examine the task that befalls each of these three—the Glover tower, the Gay Lussac tower and the lead-chambers.

The gases that come from the pyrite-furnace consist of a mixture of sulphur dioxide and air, a larger proportion of the latter than is required for the oxidation. They have a temperature of about 300°, when they enter the Glover tower, *A*, at the opening,  $\omega$ . The gas current rising in the tower meets an acid mixture flowing down from above. The latter consists of the nitroso acid from the Gay Lussac tower, diluted with the acid (*chamber-acid*) which collects in the lead-chambers, and a little nitric acid—this latter to replace the nitrogen oxides lost in the process. By means of the Glover tower the following is accomplished: In the first place, the acid which flows out from the tower contains only traces of nitroso products (§ 128); these are volatilized and carried off

with the hot gases coming from the pyrite furnace. In the second place, the sulphuric acid is relieved of some of the water with which it was diluted, the water being carried off as steam by the passing gas current. The acid has a concentration of  $60^{\circ}$ – $62^{\circ}$  BAUMÉ at the bottom. In the third place, the gases are cooled down to  $60^{\circ}$ – $80^{\circ}$  during the passage through the tower, and arrive at the top of it in just the right condition for the formation of sulphuric acid; the Glover tower therefore yields a quantity of acid equal to at least one-tenth of the product formed in the chambers.

From the Glover tower the gas mixture, now consisting of nitrogen oxides, steam and sulphurous oxide, goes to the first chamber, in which, as well as in the second, the above reactions are carried out. The third chamber serves principally to cool and dry the gases before they reach the Gay Lussac tower; on this account it is not supplied with a steam-pipe either.

When the gases leave the third chamber, they still contain nitroso products, which cannot be allowed to escape without loss. The Gay Lussac tower serves for the purpose of retaining these by letting them dissolve in  $62^{\circ}$  BAUMÉ acid. The gases are led in at the bottom of the tower through the tube, *tt'*; they give up their nitrogen oxides to the sulphuric acid with which the coke piled up in the tower, as above described, is coated, and escape through the tube, *r*, which opens into the great chimney. By means of the latter a powerful draft is maintained throughout the entire plant.

(3) The acid produced in the chambers contains about 67%  $H_2SO_4$  ( $53^{\circ}$  BAUMÉ). In this condition it is employed directly in the manufacture of fertilizers (“superphosphate”). For almost all other purposes it must first be concentrated. Ordinary sulphuric acid of commerce is of about  $66^{\circ}$  B. (B. = BAUMÉ), i.e. 96–98%  $H_2SO_4$ . It is prepared from the chamber-acid by evaporating it first in lead pans to about 78% ( $60^{\circ}$  B.) and finally in a platinum vessel.

This crude sulphuric acid of commerce (“oil of vitriol”) still contains various impurities and is usually more or less brown in color because of bits of straw (from the packing of the carboys) falling in and charring. It can be purified by diluting it, whereupon the dissolved lead sulphate is precipitated, and then stirring in a little barium sulphide. The latter produces insoluble barium sulphate, and also hydrogen sulphide, which precipitates any



arsenic or lead (§ 206) still present. The acid is then decanted from the deposit, concentrated, and finally distilled.

The contact process.—It has already been stated that sulphur dioxide unites with oxygen directly to form the trioxide and that the combination is considerably accelerated by the catalytic influence of platinized asbestos. This simple reaction is the basis of the "contact process." In practice, however, air is used instead of pure oxygen.

The process falls into four separate parts: 1. The preparation of a mixture of sulphur dioxide and air; 2. The purification of this mixture; 3. The formation of the trioxide; 4. The combination of sulphur trioxide with water to form sulphuric acid.

(1) The purification of the gas mixture is much the same as in the lead-chamber process. For reasons which will soon be made clear it is found necessary to conduct the roasting in the presence of a large excess of oxygen. While the equation



demands only 1 vol.  $\text{O}_2$  for each 2 vols.  $\text{SO}_2$ , the gases are usually mixed in the ratio of 3 vols.  $\text{O}_2$  to 2 vols.  $\text{SO}_2$ .

(2) The platinized asbestos acts efficiently only when the furnace-gases are absolutely pure, i.e., when the mixture consists simply of sulphur dioxide and air. The complete purification of these gases has been a problem of exceptional difficulty, but has been accomplished through the perseverance of KNIETSCH of the "Badische Anilin- und Sodafabrik," the great chemical factory at Mannheim, Germany. In the first place the furnace-gases must be wholly freed from dust, else the catalyzer would soon become so coated as to lose its activity. In order to determine when the gas is really dust-free it is subjected to the "optical test," i.e., it is passed through a tube closed at both ends with glass, and is examined with the eye to see whether it is perfectly transparent and free from nebulous masses. Even when this optical test is quite satisfactory the catalyzer suffers a loss in activity, if the gas is not entirely free from arsenic compounds; the least traces of the latter have an injurious effect. The presence of arsenic compounds in the furnace-gas is due to the occurrence of arsenic in the pyrites (86, 1) used for roasting. KNIETSCH has finally succeeded in completely eliminating the arsenic compounds by blowing steam into the gas mixture.

(3) Since sulphur trioxide dissociates at a high temperature into the dioxide and oxygen, the formation of it from these two gases is a reversible process:



If the pressure of the dioxide in the state of equilibrium is represented by  $p_1$ , that of the oxygen by  $p_2$ , and that of the trioxide by  $p_3$ , the equilibrium equation must be:

$$p_1^2 p_2 = k p_3^2,$$

where  $k$  stands for the equilibrium constant. According to this equation the formation of sulphur trioxide is more complete in the presence of an excess of either sulphur dioxide or oxygen, for as  $p_1$  or  $p_2$  increases  $p_3$  must also increase. Since the object in view is to convert the dioxide as completely as possible into the trioxide, it is advantageous to provide a large excess of oxygen. This explains why more than the theoretical amount of oxygen is taken. Cf. (1).

The equilibrium must also depend on the pressure, for, if this is increased  $n$  times, the equation becomes:

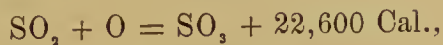
$$(np_1)^2 np_2 = Kn^2 p_3^2, \quad \text{or} \quad np_1^2 p_2 = Kp_3^2,$$

from which it is evident that at a higher pressure ( $n > 1$ ) the formation of the trioxide is more nearly complete. The manufacturer does not find it necessary, however, to employ high pressure, which would involve, moreover, a great complication of the apparatus.

Finally, the influence of temperature must be mentioned. Sulphur dioxide unites with oxygen easily at  $400^\circ$ . When equilibrium is established in the system  $2\text{SO}_2 \rightleftharpoons 2\text{SO}_3 + \text{O}_2$  at this temperature, the left-hand side predominates. If the temperature is raised, the quantity of trioxide formed diminishes, at first slowly, but between  $600^\circ$  and  $800^\circ$  more rapidly, until at  $1000^\circ$  the dissociation of sulphur trioxide is complete and it can no longer be formed. These temperatures hold for a mixture of sulphur dioxide and so much air that the relation  $\text{SO}_2 : \text{O}_2$  is as 2:3, assuming that the pressure is the ordinary one.

If it is desired that the combination of sulphur dioxide and oxygen should be as complete as possible, the temperature must be

kept at about  $400^{\circ}$ . Since, however, the heat of formation of the trioxide is great, viz.,



the apparatus must be cooled. This is done most practicably by the aid of a fresh portion of the gas mixture, as the next paragraph sets forth.

The construction of the apparatus is as follows: The tubes *ab* (Fig. 39) contain the platinized asbestos *b*, supported on little sieves (shown in the middle tubes). The purified furnace-gases first pass

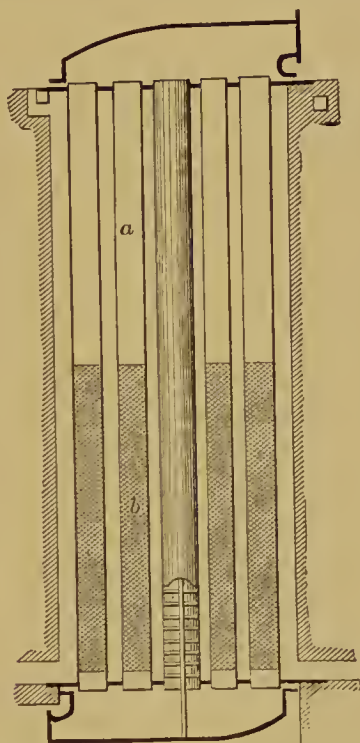


FIG. 39.—CONTACT PROCESS APPARATUS.

around the outside of the tubes and are thus warmed to the desired temperature at the heat expense of the gas system within. When the proper temperature is reached the gases are allowed to enter the tubes, where sulphur trioxide is formed with the evolution of more heat. By increasing or diminishing the rate of flow of the gas current the temperature can be regulated very satisfactorily. When the operation is started the apparatus must first be warmed to  $400^{\circ}$ .

(4) The reaction between sulphur trioxide and water is an energetic one. Nevertheless, the manufacture of sulphuric acid from these two compounds involved some difficulty, inasmuch as

sulphur trioxide fumes invariably escaped when this substance was introduced into water or dilute sulphuric acid. Only when sulphuric acid of 97–98% is used as the absorbent and care is taken to keep the acid at this concentration by the simultaneous addition of water does a complete and immediate absorption occur.

This is due to two circumstances: first, that traces of water change sulphur trioxide into the asbestic modification (79), which is only slowly absorbed by sulphuric acid; second, that at the concentration of 97–98%  $H_2SO_4$  the system  $xSO_3 + yH_2O$  has a minimum of vapor tension, which is very low.

**87. Physical Properties.**—The pure compound, hydrogen sulphate, is an oily liquid at ordinary temperatures, solidifying at a low temperature and melting again at  $+10.5^\circ$ . Its specific gravity in the liquid state ( $15^\circ$ ) is 1.8372.

**Chemical Properties.**—The concentrated acid obtained by distillation is not the simple compound  $H_2SO_4$ , for it still contains about 1.5% of water. In order to prepare the absolutely pure acid the distilled product must be mixed with the theoretical amount of sulphur trioxide. When pure sulphuric acid is heated, it begins at  $30^\circ$  to give off fumes of sulphur trioxide; this continues until the boiling-point,  $338^\circ$ , is reached, when an acid with 1.5% water distills over, having a specific gravity of 1.842 at  $15^\circ$ , that is, higher than that of the pure compound. On heating the vapor of sulphuric acid above the boiling-point, it begins to break up into water and the anhydride; this dissociation is complete at  $450^\circ$ , for the vapor density at that temperature is found to be 25.1, while that of  $SO_3 + H_2O$  is theoretically 24.5.

When sulphuric acid is mixed with water, a strong evolution of heat occurs. The mixing must therefore be done with great care, particularly in glass vessels, the acid being poured in a fine stream into the water and the liquid being steadily stirred. On mixing them in the reverse way, by pouring the water into the sulphuric acid, the intense heat that is produced may cause the glass to crack. However, when the acid is mixed with ice in a certain proportion, a strong cooling follows.

The mixing of sulphuric acid and water is attended by a contraction, i.e. the volume of the dilute acid is smaller than the sum of the volumes of water and acid.

Sulphuric acid is able to form hydrates with water. A

mixture of the same number of gram-molecules of acid and water congeals on cooling; the hydrate formed melts at  $7.5^{\circ}$  and has the composition  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ . Still other hydrates are known also.

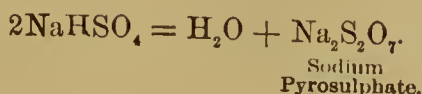
Sulphuric acid is a strong dibasic acid; even in a moderately diluted state (e.g. in  $\frac{1}{10}$  normal solution, *cf.* § 93) it is almost wholly dissociated into  $\text{H}^+$  and  $\text{HSO}_4'$  ions (see § 81). It acts on many metals, giving off hydrogen. This action is made use of, as stated above, in the preparation of hydrogen; the acid must, however, be dilute, for when it is too strong or warmed, the hydrogen generated partially reduces the sulphuric acid so that the gas given off contains hydrogen sulphide. Sulphur dioxide also is formed when hydrogen is led into hot sulphuric acid. It is upon this action that the reaction of copper with hot concentrated sulphuric acid depends (§ 78). Mercury, silver and certain other metals are similar to copper in their behavior. Platinum and gold are not attacked by the acid.

Sulphuric acid makes holes in paper, linen, dress goods and the like, when dropped on them. It has a destructive, charring effect on organic substances in general. This is due on the one hand to the great tendency of the acid to unite with water, which makes it not only deprive other substances of the water they contain, but also withdraw the hydrogen and oxygen from organic compounds to form water. On the other hand, sulphuric acid gives up oxygen to many organic substances, being itself reduced.

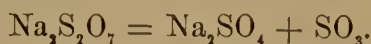
In order to detect free sulphuric acid in vinegar, for example, the liquid is evaporated on a water-bath with a little sugar. Free sulphuric acid, if present, chars the sugar during the concentration.

The most of the salts of sulphuric acid (sulphates) are soluble in water. Barium, strontium and lead sulphates are insoluble, while calcium sulphate (gypsum) is slightly soluble, but only to a very small degree. The formation of barium sulphate,  $\text{BaSO}_4$ , serves as a *characteristic test for sulphuric acid*, or, as we may better say, for the *ion*,  $\text{SO}_4''$ .

The sulphates are in general very stable. They can, for instance, be heated to very high temperatures without decomposition. The acid salts lose water on heating, and pass over into **pyrosulphates**:



If these pyrosulphates are heated still higher, they give off sulphur trioxide and form neutral salts:



**88. Uses.**—Sulphuric acid is of enormous practical value, its uses being most varied. It is employed in the preparation of almost all other mineral acids from the salts. In the manufacture of soda after LE BLANC it is used in astonishingly large amounts and in almost all other branches of chemical industry it is of some service or other. In the laboratory it is often employed as a drying-agent. A moist substance is dried very thoroughly when placed in a closed apparatus near a dish of the concentrated acid. For this purpose special pieces of apparatus are constructed, called *desiccators*.

The *determination of the concentration* of sulphuric acid is an operation that is frequently necessary. Ordinarily the specific gravity is made use of, for this can be determined rapidly with an areometer. There are tables so prepared that the proportion of  $\text{H}_2\text{SO}_4$  or  $\text{SO}_3$  in a dilute acid whose specific gravity and temperature are known can be quickly read. BAUMÉ, a chemist of the latter part of the eighteenth century, constructed an areometer with an arbitrary scale, the zero-point of which indicates pure water and the point 10 being reached in a 10% salt-solution. All the divisions are equal. 100%  $\text{H}_2\text{SO}_4$  would then be represented by the line 66.6. In the arts the strength of sulphuric acid is still given as so many “degrees BAUMÉ.”

#### Fuming Sulphuric Acid.

**89.** This is the name of a sulphuric acid that contains sulphur trioxide in solution. It is obtained by dissolving the oxide in concentrated sulphuric acid.

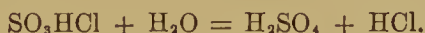
Fuming sulphuric acid is a thick oily liquid, which fumes vigorously in the air, throwing off the trioxide. Sp. g. = 1.85–1.90. On cooling it pyrosulphuric acid ( $\text{H}_2\text{S}_2\text{O}_7 = \text{H}_2\text{SO}_4 + \text{SO}_3$ ) crystallizes out. Some salts of the latter are also known (§ 87). It forms large colorless crystals, that melt at 35°. Pyrosulphuric acid dissociates even at ordinary temperatures, and on gently warming breaks up completely into sulphuric acid and trioxide. Besides pyrosulphuric acid several other compounds of water and sulphur trioxide are known.

## CHLORIDES OF SULPHURIC ACID.

90. When phosphorus pentachloride acts on sulphuric acid a compound  $\text{SO}_3\text{HCl}$ , chlorosulphonic acid, is formed :



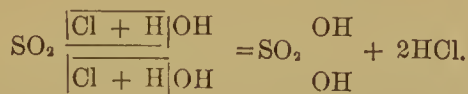
The same compound results from the direct union of sulphur trioxide and hydrochloric acid. It is a colorless liquid, which fumes vigorously on exposure to the air. Sp. g. = 1.766 at  $18^\circ$ . Boiling-point,  $158^\circ$ . On the addition of water a violent reaction occurs, producing hydrochloric acid and sulphuric acid :



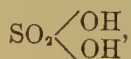
A compound,  $\text{SO}_2\text{Cl}_2$ , sulphuryl chloride, is obtained by the direct union of sulphur dioxide and chlorine, most easily by first saturating camphor with sulphur dioxide (which readily dissolves in it) and then passing chlorine over it. The camphor remains unchanged. Sulphuryl chloride is a colorless liquid, which boils at  $69.1^\circ$ , has a penetrating odor, fumes strongly in the air and has a specific gravity of 1.6674 at  $20^\circ$ . The addition of a little water converts it into chlorosulphonic acid and hydrochloric acid, much water to sulphuric and hydrochloric acids :



These decompositions of sulphuryl chloride can be represented in the following way :



In the place of the two chlorine atoms we have, therefore, two OH (*hydroxyl*) groups entering. For this reason it is assumed, in close analogy with the methods of organic chemistry, that sulphuric acid contains two hydroxyl groups. From this it follows that the arrangement of the atoms in the molecule of sulphuric acid may be represented by the diagram :

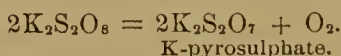


in which the  $\text{SO}_2$  (*sulphuryl*) group is joined to two hydroxyls. Such a diagram is known as a **structural**, or **constitutional**, formula.

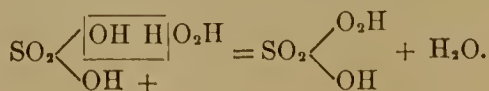
For sulphurous acid,  $\text{H}_2\text{SO}_3$ , the analogous structural formula would be:  $\text{SO} \begin{matrix} \diagup \text{OH} \\ \diagdown \text{OH} \end{matrix}$ . As a matter of fact, organic derivatives of this acid (esters) are known which can be derived from an acid of this constitution. For the salts of sulphurous acid, however, another structure must be assumed, viz.:  $\text{SO}_2 \begin{matrix} \diagup \text{H} \\ \diagdown \text{OH} \end{matrix}$ . In organic chemistry arguments are to be found for this asymmetrical constitution of sulphurous acid salts.

#### Persulphuric Acid, $\text{H}_2\text{S}_2\text{O}_8$ .

91. The potassium salt,  $\text{K}_2\text{S}_2\text{O}_8$ , of this acid can be obtained by the electrolysis of a cold saturated solution of potassium sulphate,  $\text{K}_2\text{SO}_4$ , in sulphuric acid of 1.3 sp. g. In such a solution we may assume we have the ions  $\text{H}^+$  and  $\text{KSO}_4^-$ ; the latter are discharged at the anode and can then unite to form  $\text{K}_2\text{S}_2\text{O}_8$ , which is difficultly soluble and separates out as a white crystalline mass. However, the combination of two  $\text{KSO}_4$  groups only takes place when their concentration at the anode is quite high; for if this is not the case there is more opportunity for secondary reactions, for instance, to unite with water to form  $2\text{KHSO}_4$  and  $2\text{OH}$ , the latter of which is decomposed into  $\text{H}_2\text{O}$  and  $\text{O}$ . Such a high concentration at the anode is reached by using a very small electrode. The electric current therefore has a high density at the anode, that is, a large quantity of electricity must pass through a small surface. The effect thereof is, that this large quantity discharges a great many  $\text{KSO}_4^-$  ions into a small space, or in other words, produces enough  $\text{KSO}_4$  groups to make the concentration very high there. As low as  $100^\circ$  it decomposes in the following way:



The barium salt of persulphuric acid is soluble in water, as are also most of the other known salts. The solution of potassium persulphate in sulphuric acid is called CARO'S *liquid*. It probably contains a compound  $\text{H}_2\text{SO}_5$  ( $= \text{SO}_2 \begin{matrix} \diagup \text{OH} \\ \diagdown \text{O}_2\text{H} \end{matrix}$ ), because a liquid with the same reactions is obtained by mixing hydrogen peroxide with an excess of strong sulphuric acid:



This compound is called by BAEYER sulphomonoper-acid; it has very strong oxidizing powers. It sets iodine free from potassium iodide, ox-



idizes sulphur dioxide to trioxide, and ferrous to ferric salts and also precipitates the higher oxides of silver, copper, manganese, cobalt and nickel from solutions of salts of these metals. On the other hand, it neither bleaches permanganate solution nor oxidizes solutions of chromic and titanio acids; in these respects it is distinguished from hydrogen peroxide (called by BAEYER hydroperoxide), to which it otherwise shows much similarity.

#### POLYTHIONIC ACIDS.

92. Under this name are grouped four acids of the general formula  $H_2S_nO_6$ , in which the number of sulphur atoms,  $n$ , can be 2, 3, 4 and 5, and this determines the names of the individual acids.

**Dithionic acid,  $H_2S_2O_6$ .** The manganese salt of this acid is obtained when finely powdered manganese dioxide is suspended in water and sulphurous oxide passed in :



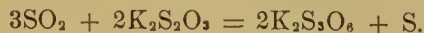
At the same time a little sulphuric acid is formed. Baryta water is added to the solution to precipitate the sulphuric acid as barium sulphate and convert the manganese salt into barium dithionate :



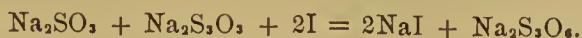
From this barium salt the dithionic acid can be liberated by sulphuric acid. The solution can be concentrated in vacuo over sulphuric acid till its specific gravity reaches 1.347; farther concentration or warming results in a decomposition :



**Trithionic acid,  $H_2S_3O_6$ .** Potassium trithionate is formed when a solution of potassium thiosulphate is saturated with sulphur dioxide :



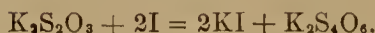
The compound is also formed when a solution of equimolecular amounts of sodium sulphite and thiosulphate are treated with iodine :



The free acid is unstable; even at ordinary temperatures it decomposes in a dilute solution into sulphur, sulphurous oxide and sulphuric acid:



**Tetrathionic acid.** Its salts result from the action of iodine on the solution of a thiosulphate.



The acid itself can be obtained by adding sulphuric acid to the barium salt, which is prepared in an analogous manner; also only in dilute solution. In the latter condition it is quite stable; in the concentrated state it breaks up into sulphur, sulphurous oxide and sulphuric acid.

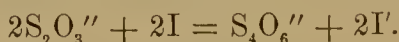
**Pentathionic acid.** On mixing solutions of sulphur dioxide and hydrogen sulphide the principal reaction is a mutual oxidation and reduction of these compounds with the separation of sulphur (§78). The action is, however, much more complicated, inasmuch as polythionic acids, among them pentathionic acid, are formed in addition at the same time. The mixture of  $\text{H}_2\text{S}$  aq and  $\text{SO}_2$  aq is known as "WACKENRODER'S liquid." Well-crystallized salts of pentathionic acid have been prepared.

#### Use of Sodium Thiosulphate in Volumetric Analysis. Iodometry.

**93.** On adding sodium thiosulphate to an iodine solution, the intensely brown liquid loses its color, sodium iodide and sodium tetrathionate, two colorless compounds, being formed:



or writing only the ions that take part in the reaction:



The disappearance of the color is thus due to the fact that the molecules of I are transformed into ions by taking up two negative charges from  $2\text{S}_2\text{O}_3''$ . Upon this fact a method is based for determining the amount of free iodine in a solution. This is done by allowing a solution of sodium thiosulphate whose concentration (*titre*) is known flow drop by drop into a definite volume of iodine solution. [For letting out a certain amount of liquid a pipette (Fig. 40) is commonly employed.] The color gradually brightens and finally a point is reached when the liquid is only slightly tinged and the addition of another drop causes the color to entirely disappear. This transition can be very accurately detected. The iodine molecules have now entirely disappeared. Since according

to the above equation a molecule of thiosulphate is consumed for each atom of iodine, the percentage of iodine in the solution can be calculated from the amount of thiosulphate used.

To make the calculation of the result of such a determination (*titration*) as easy as possible the thiosulphate solution is so *standardized* that it bears a certain relation to an equivalent of iodine (= 127 g.), i.e. a certain amount bleaches exactly this much iodine.

“**Normal solution**” is a name applied to a solution containing the equivalent weight (§ 23) in grams (*gram equivalent*) in one liter. Frequently use is also made of a  $\frac{1}{2}$ ,  $\frac{1}{4}$ ,  $\frac{1}{10}$  or a twice, thrice,



FIG. 40. PIPETTE.



FIG. 41.—BURETTE.

etc., normal solution. A normal hydrochloric acid contains 36.5 g. HCl, a normal sulphuric acid 49 g.  $H_2SO_4$  (=  $\frac{1}{2}$  gram-molecule), a normal iodine solution 127 g. iodine, per liter. Detailed directions for preparing such solutions can be found in the text-books on analytical chemistry.

In order to determine readily the volume of thiosulphate solution that is required in the analysis, use is made of a burette (Fig. 41), a glass tube that is divided into  $\frac{1}{10}$  c.c. and closed at the lower end with a glass stop-cock or with a rubber tube and pinch-clamp. In titrating the iodine solution the thiosulphate solution is allowed to flow out slowly and, finally, drop by drop while the liquid is being stirred.

*Example.* For 50 c.c. of an iodine solution whose strength is to be determined 27.30 c.c.  $\frac{1}{10}$  normal thiosulphate solution were necessary before all color had finally disappeared. Required the number of grams of iodine contained in 1 liter of this solution.

1000 e.c.  $\frac{1}{10}$  normal  $\text{Na}_2\text{S}_2\text{O}_3$  solution (see above) decolorizes  $\frac{1}{10}$  equivalent of iodine (= 12.7 g.); 27.3 c.c. therefore decolorizes  $27.3 \times \frac{12.7}{1000}$  g. iodine. This amount is contained in 50 c.c. of the iodine solution in question. Hence 1 liter of the latter contains  $20 \times 27.3 \times 12.7 \times 10^{-3} = 6.8842$  g. iodine.

Various other substances which liberate iodine from potassium iodide can be determined by titrating the amount of iodine displaced; for example, chlorine and bromine may be thus determined, since they set free the equivalent amount of iodine from potassium iodide solution.

## SELENIUM AND TELLURIUM.

94. Selenium was discovered by BERZELIUS in 1817. It took its name from  $\sigma\epsilon\lambda\acute{\eta}\nu\eta$  (the moon), because it possesses great similarity to the element tellurium (named from *tellus* = the earth) discovered a short time previous. It is rather widely distributed in nature; occurs, however, only in small quantities. It is frequently found in pyrite and also appears in some rare minerals. When this sort of pyrite is employed in sulphuric acid manufacture, the selenium collects in the "chamber-mud" of the lead-chambers; from this it is usually obtained.

The process is as follows: The selenium deposit is heated with nitric acid, which oxidizes the selenium to selenic acid,  $\text{H}_2\text{SeO}_4$ . The solution thus obtained is first boiled with hydrochloric acid, whereby selenous acid,  $\text{H}_2\text{SeO}_3$ , is formed with the evolution of chlorine. This latter acid is then reduced by means of sulphurous oxide to selenium, which separates in amorphous red flakes.

Selenium displays analogy with sulphur in many respects; for instance, in occurring in various allotropic conditions. According to SAUNDERS, there is an amorphous red modification, that is soluble in carbon bisulphide; it separates from this solution in the form of a second modification which is the red crystalline selenium, fusing at  $170^{\circ}$ – $180^{\circ}$ . Then there is a metallic form fusing at  $217^{\circ}$ . This modification appears when amorphous selenium is heated to  $97^{\circ}$ , at which point a sudden and marked rise of temperature occurs; or when molten selenium is suddenly cooled to  $210^{\circ}$  and kept for a time at this temperature. In this metallic state selenium has a metallic lustre, is insoluble in carbon bisulphide and conducts electricity. Its conductivity strangely depends very much on the intensity of its illumination, however.

The melting-point of selenium is at  $217^{\circ}$ , its boiling-point at  $680^{\circ}$ . As in the case of sulphur the vapor density decreases with rising temperature till about  $1400^{\circ}$  is reached, when it remains constant. At this temperature it is found to be 81.5 ( $H = 1$ ), corresponding to a molecular weight of 163.0. Now since the atomic weight of selenium, as deduced from the vapor density of its compounds, is 78.9, the above molecular weight agrees very closely with the formula  $Se_2$ .

**Hydrogen selenide**,  $H_2Se$ , can be obtained directly from its elements, as these unite at  $400^{\circ}$ . Analogously to hydrogen sulphide, it can also be gotten by the decomposition of iron selenide,  $FeSe$ , with hydrochloric acid. At a high temperature hydrogen selenide dissociates into its elements. Its properties are only slightly acidic and it is more poisonous than sulphuretted hydrogen. The heavy metals are precipitated from their solutions as selenides by it.

An aqueous  $H_2Se$  solution becomes turbid on standing because of the selenium that has separated out.

Two **chlorine compounds**,  $Se_2Cl_2$  and  $SeCl_4$ , are known. The latter is much more stable than the corresponding sulphur compound,  $SCl_4$  (§ 75). Selenium tetrachloride is solid and sublimes without decomposition; dissociation does not begin until  $200^{\circ}$  is reached.

**Selenium dioxide**,  $SeO_2$ , is the only oxide of selenium known. It results from the burning of selenium in the air. The extremely disagreeable odor which arises is not a property of the dioxide,

however, but is probably due to the formation of another oxygen compound of selenium which has not as yet been isolated. Selenium dioxide forms long white needles that sublime at  $310^{\circ}$ .

Selenium dioxide is an acid anhydride; on dissolving it in water an acid, **selenious acid**,  $\text{H}_2\text{SeO}_3$ , is formed, which can be isolated (unlike sulphurous acid). This acid crystallizes in large colorless prisms. On heating it breaks up into water and anhydride. Sulphur dioxide or stannous chloride reduce it to free selenium, which is deposited in red flakes:



Sulphuretted hydrogen precipitates from the solution selenium sulphide,  $\text{SeS}$ , insoluble in ammonium sulphide.

When chlorine is passed into the solution of selenious acid or when bromine is added to it, **selenic acid**,  $\text{H}_2\text{SeO}_4$ , is formed. In the pure state this is a crystalline solid, melting at  $58^{\circ}$ . The 95% solution of it is an oily liquid, which has the appearance of sulphuric acid. The barium salt of the acid, like that of sulphuric acid, is extremely difficultly soluble.

On boiling with hydrochloric acid, selenic acid is reduced to selenious acid with the evolution of chlorine.

## Tellurium.

**95.** Tellurium is of rare occurrence; it is known in the native condition and also in combination with bismuth, and with gold or silver (in sylvanite, or *graphic tellurium*). It is found chiefly in Transylvania and in the Altai mountains, and also in Boulder Co., Colorado. In the amorphous condition tellurium is a black powder, but after fusion it is silvery white, of a metallic lustre and a conductor of heat and electricity. The vapor density, as in the cases of selenium and sulphur, decreases with increasing temperature and does not remain constant till about  $1400^{\circ}$ ; it then corresponds to a  $\text{Te}_2$  molecule.

**Hydrogen telluride**,  $\text{H}_2\text{Te}$ , results from the action of hydrochloric acid on zinc telluride,  $\text{ZnTe}$ . The product thus obtained contains more or less hydrogen. It is very poisonous, and dissociates readily. From solutions of the heavy metals it precipitates their tellurium compounds (tellurides).

**Tellurium dioxide**,  $\text{TeO}_2$ , is formed on burning tellurium in the air. It is very difficultly soluble in water.

**Tellurous acid**,  $\text{H}_2\text{TeO}_3$ , is obtained by dissolving tellurium in nitric acid. It dissolves in water with great difficulty and breaks up on warming into  $\text{TeO}_2$  and  $\text{H}_2\text{O}$ .

**Telluric acid**,  $\text{H}_2\text{TeO}_4$ , is prepared by fusing the metal or the dioxide with soda and saltpetre and separating the acid from the tellurate formed. The compound  $\text{H}_2\text{TeO}_4 + 2\text{H}_2\text{O}$  crystallizes out from the aqueous solution; it loses its water of crystallization at  $100^\circ$ . The free telluric acid,  $\text{H}_2\text{TeO}_4$ , prepared in this way is a white powder, difficultly soluble in cold water. Telluric acid has only weakly acid properties.

Selenium and tellurium both combine with potassium cyanide, when they are fused with it, compounds corresponding to  $\text{KCNS}$ , viz.,  $\text{KCNSe}$  and  $\text{KCNTe}$ , being formed. Nevertheless, while potassium tellurio-cyanide is at once decomposed by the oxygen of the air with the separation of tellurium, potassium selenio-cyanide is more stable and does not decompose with the separation of selenium until it is boiled with hydrochloric acid. We have here a means of detecting selenium in the presence of tellurium and of separating the two.

### SUMMARY OF THE OXYGEN GROUP.

96. The elements oxygen, sulphur, selenium and tellurium, like the halogens, form a natural group, particularly in two respects; their compounds correspond to a general type and their physical and chemical properties vary gradually with increasing atomic weight. Their hydrogen compounds have the formula  $\text{RH}_2$ , their oxygen compounds and their acids the formulæ  $\text{RO}_2$  and  $\text{H}_2\text{RO}_3$ , and also  $\text{RO}_3$  and  $\text{H}_2\text{RO}_4$ . Ozone may be considered with reference to these types as analogous to sulphur dioxide;  $\text{O}\cdot\text{O}_2$  ozone,  $\text{S}\cdot\text{O}_2$  sulphur dioxide.

The following table shows the gradual change, or progression, of the physical properties:

	O.	S.	Se.	Te.
Atomic weight.....	16.00	32.06	79.07	127
Specific gravity.....	1.124 (at $-181^\circ$ )	1.95-2.07	4.2-4.8	6.2
Melting-point.....	.....	$114.5^\circ$	$217^\circ$	$452^\circ$
Boiling-point.....	$-181.4^\circ$	$450^\circ$	$680^\circ$	white heat
Color.....	light blue.	yellow.	red.	black.

As the atomic weight increases, the values of the physical constants also increase, as the table shows. At the same time the

external appearance approaches that of the metals; in tellurium the metallic appearance is quite marked.

The *instability of the hydrogen compounds* increases from oxygen to tellurium; the *strength of the oxygen acids* diminishes rapidly, sulphuric acid belonging to the strongest, and telluric acid to the very weak, acids.

It should also be noted that all of these elements appear in allotropic modifications.

### THERMOCHEMISTRY.

97. It was stated above (§ 20) that a chemical combination or decomposition is accompanied by an evolution or absorption of heat, in other words by a heat-change, or **caloric effect**. In many cases this caloric effect has been carefully measured. The work of BERTHELOT and of THOMSEN along this line has been especially fruitful. That part of chemistry which deals particularly with these caloric effects is called *thermochemistry*.

The caloric effect is always given for molecular amounts of the reacting substances, since in this way only is it possible to compare substances from a chemical standpoint. Hence, when the **heat of formation** of water is said to be 69.0 calories (kilogram-calories), it is implied that this number of calories is evolved by the union of 2 g. hydrogen with 16 g. oxygen:



In this equation H and O stand for gram-atoms. In expressing a caloric effect it is necessary to indicate the state of matter the reacting and the resulting substances are in, in so far as this is not self-evident, because the latent heat of fusion or vaporization must be taken into consideration.

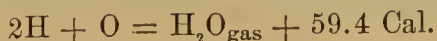
The above amount,



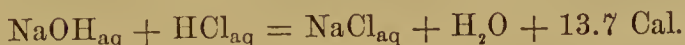
refers to the formation of water and its conversion to a liquid. It therefore includes the heat of condensation. Since this amounts to 0.536 Cal. per gram, it would in this case (for 18 g.) be 9.6 Cal.;



hence the caloric effect of the combustion of hydrogen to steam at 100° is



The caloric effect is also influenced by the condition, whether solid or dissolved, in which the substances react, inasmuch as solution is almost always accompanied by a heat-change. In the formation of sodium chloride by the mixture of dilute solutions of sodium hydroxide and hydrochloric acid (this being indicated by aq after the formulæ of the substances) the caloric effect is:



When the salt is, however, prepared by passing hydrochloric acid gas into a dilute solution of the base, the equation is as follows:



We thus obtain 13.7 Cal. as before, but increased by the heat of solution of gaseous hydrochloric acid in a large amount of water, viz., 17.4 Cal.

The heat of formation of chemical compounds must be equal to their heat of decomposition, but have the opposite sign. Were this not the case, heat would be lost or gained when a compound is formed and then decomposed so as to return to the original condition, and such a result would be at variance with the Law of the Conservation of Energy.

In many instances a distinction must be made between *heat-changes* and *energy-changes* in a reaction, particularly wherever positive or negative work is done on the system from without. For example, work is performed by the surroundings when the reaction takes place under atmospheric pressure, and is attended by a decrease of volume. In this instance the heat evolved,  $W$ , represents the sum of the energy produced,  $E$ , and the work,  $A$ , performed from without.  $W = E + A$ . In the case of reactions attended by an increase of volume under constant pressure  $A$  is negative, hence  $W = E - A$ .

The difference between the evolution of heat and of energy in such cases is not always to be overlooked, especially when the change of volume is a result of the increase or diminution of the number of gas molecules. In

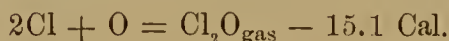
that case the difference is considerable, but is easily calculated. The evolution of heat amounts to 0.6 Cal. more than the energy given off for each gram-molecule of gas that disappears in the reaction (i.e. over and above any new gas produced).

Energy generated,  $2\text{H} + \text{O} - \text{H}_2\text{O}_{\text{liquid}} = 69.0 \text{ Cal.}$

Heat generated,  $2\text{H} + \text{O} - \text{H}_2\text{O}_{\text{liquid}} = 69.9 \text{ Cal.}$

The difference, + 0.9 Cal., is due to the disappearance of  $1\frac{1}{2}$  gram-molecules of gas.

Experience has shown that in the formation of most compounds heat is generated, but that in many cases heat is absorbed. Chemical actions of the first sort are called **exothermic**, those of the second **endothermic**, reactions. An example of the second sort is the synthesis of chlorine monoxide:



98. For the **determination of the caloric effect** various methods are in use. Only those actions are suitable for thermochemical measurements which complete themselves quickly. In measuring the caloric effect in the case of liquids or solutions, as, for example, the **heat of neutralization** of acids and bases, the **heat of solution** or of dilution, etc., an ordinary calorimeter is generally used, such as is employed in physics for the method of mixtures, the same precautions being taken in order to secure accurate results.

The **heat of combustion** of a substance is usually measured with the *calorimetric bomb* of BERTHELOT-MAHLER. This is the usual method with organic compounds.

99. **The Law of HESS.** *The entire caloric effect (the whole amount of energy) produced by the transformation of one chemical system into another is independent of all intermediate stages.*

This law is a direct consequence of the principle of the conservation of energy. If it were not valid, energy would have to be gained or lost in the transition from one system to another and the subsequent return to the initial condition, which is contradictory to the above principle. A few examples will serve to make this law clearer.

(a) A dilute solution of sodium sulphate can be prepared from sodium hydrate, sulphuric acid and water in various ways. For instance, two gram-molecules of the base can be treated at once



chemical study. We will then start with the system, H, S, and O, and conceive it as undergoing the following changes: (1) hydrogen and sulphur are burned to water and sulphur dioxide; (2) hydrogen and sulphur are combined and the hydrogen sulphide formed is burned to water and sulphur dioxide. Since we started with the same system and in the end reached the same result in each case, the caloric effect must be the same according to HESS'S law. We therefore have:

$$\begin{aligned} \text{Heat of combustion of H} + \text{heat of combustion of S} &= \\ \text{heat of formation of H}_2\text{S} + \text{heat of combustion of H}_2\text{S}. & \\ (2\text{H} + \text{O} - \text{H}_2\text{O}) + (\text{S} + 2\text{O} - \text{SO}_2) &= \\ (2\text{H} + \text{S} - \text{H}_2\text{S}) + (\text{H}_2\text{S} + 3\text{O} - \text{SO}_2 - \text{H}_2\text{O}). & \\ 69.0 + 69.26 = x + 133.46; & \\ \therefore x = (\text{S} + 2\text{H} - \text{H}_2\text{S}) = 4.8. & \end{aligned}$$

It is a somewhat more complicated task to determine the heat of formation of hypochlorous acid, an example of a compound that cannot be prepared directly from its elements. It is computed in the following way: When a solution of this acid is mixed with hydriodic acid, it decomposes according to the following equation:



This amount of heat evolved is the algebraic sum of the following caloric effects: (1) decomposition of  $\text{HOCl}_{\text{aq}}$ , unknown; (2) decomposition of  $2\text{HI}_{\text{aq}} = -26.34$ ; (3) formation of  $\text{HCl}_{\text{aq}} = 39.4$ ; (4) formation of water = 69.0.

The equation thus becomes

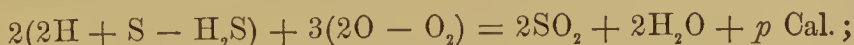
$$-x - 26.34 + 39.4 + 69.0 = 50.41;$$

and

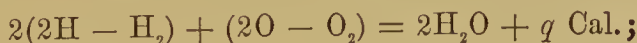
$$x = +31.65 \text{ Cal.}$$

100. In using these values of the heat of formation and heat of decomposition it should be noted that they do not represent the amounts of heat liberated by the combination of atoms to form molecules, but that the heat of decomposition of the molecules of the elements (i.e. the amount of heat required to break these molecules

up into atoms) is always included. When, for example, chlorine unites with hydrogen to form hydrochloric acid, 22.0 Cal. are given off. That which is measured is the **total caloric difference** between the initial system  $H_2 + Cl_2$  and the  $2HCl$  formed from it. In the indirect determination of a heat of formation with the help of HESS'S law the calculated caloric effect also includes the heat of decomposition of the molecules of the elements. In the determination of the heat of formation of hydrogen sulphide, for instance, in the above way the caloric effect of the combustion of this gas is composed of the following parts:



that of the combustion of hydrogen of the following:



that of the combustion of sulphur of



$(2O - O_2)$ , etc., indicating the heat of decomposition of molecules of the elements.

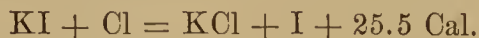
The heat of formation of hydrogen sulphide is  $r + q - p$ . Deducing the value of  $r + q - p$  from the above equations, we have

$$r + q - p = (2S - S_2) + 2(2H - H_2) - 2(2H + S - H_2S),$$

from which it follows that the heats of formation of the sulphur and hydrogen molecules are included in the heat of formation found.

101. Experience has shown that ordinarily those chemical processes take place whose results are exothermic, while those which would have an endothermic effect do not take place. This furnishes us a useful means of often foretelling the direction of a reaction. The formation of water or hydrogen chloride is accompanied by the evolution of considerable heat; that of chlorine monoxide,  $Cl_2O$ , on the contrary, is endothermic; as a matter of fact the latter sub-

stane cannot be obtained directly from its constituent elements, while this is possible with water and hydrochloric acid. Iodine is displaced from metal iodides by chlorine, chlorides and free iodine being formed. The equation is



On the other hand, iodine cannot liberate chlorine from potassium chloride, since this action would consume 25.5 Cal. Many examples could be given of reactions which might proceed in various directions, but take that one which involves an evolution of heat.

It might therefore be supposed that the heat given off in a reaction could be regarded as a measure of the affinity satisfied by it. BERTHELOT has indeed accepted this view; but reasons, furnished by thermodynamics, prove that it cannot be correct. The application of the methods of thermodynamics to chemical problems has led to correct views concerning this and many other kindred matters. It cannot, however, be denied that in its present condition thermodynamics is still far too general for the great majority of cases and that scientists are just beginning to apply its general principles to definite reactions. One of the most important deductions of thermodynamics is the phase rule (§ 71), whose applications are already numerous. Another is LE CHATELIER'S rule, which we shall next consider; many applications of it will be met with in succeeding chapters.

#### LE CHATELIER'S RULE.

**102.** *When any system is in physical or chemical equilibrium, a change in one of its equilibrium-factors produces a change in the system, which tends to oppose the former.*

This rule, or theorem, which can be called the **principle of the resistance of the reaction to the action**, furnishes us with a convenient means of foretelling in many instances the direction which a reaction will follow. Some examples may be given to illustrate the rule.

(1) When a system of water and ice is subjected to increased pressure, the ice melts; that is, that process goes on which involves

a contraction, for by this contraction the system diminishes the pressure exerted on it.

(2) Monoclinic sulphur, when compressed near the transition-point (the temperature of equilibrium for ordinary pressure), passes over into rhombic sulphur, since this process involves a lessening of volume, and in the end also a diminution of pressure, as in the previous case.

(3) When a solution is diluted the osmotic pressure decreases according to BOYLE'S law; in the case of a solution of an electrolyte dilution will be followed by farther dissociation, since this increases the osmotic pressure.

(4) When a liquid is heated, more vapor is formed; since the vaporization absorbs heat, this acts in opposition to the heat which is applied.

**103.** VAN'T HOFF'S principle of mobile equilibrium is an application of this rule to a special case. It says: *An equilibrium between two different states of matter (systems) displaces itself under constant pressure by a  $\frac{\text{fall}}{\text{rise}}$  of temperature to that one of the two systems whose formation  $\frac{\text{evolves}}{\text{absorbs}}$  heat.* A few examples will serve to make this clear.

(1) Rhombic sulphur becomes monoclinic when heated above the transition-point, since heat is absorbed by this transition. Below this temperature the inverse transition takes place. (Ordinary pressure is assumed in each case.) The reaction works in opposition to the temperature-change produced from without.

(2) A salt whose heat of solution is negative (saltpetre) dissolves to a greater degree if the temperature rises. If its heat of solution is positive, a rise of temperature causes a separation from solution (§ 235). We shall meet with still other illustrations of this rule in the remaining portion of the book.

**104.** There is still another deduction from thermodynamics worthy of notice here. Without explaining it we may say that thermodynamics furnishes in a very general way a means of determining whether or not a reaction is possible. Nevertheless it does not require that the particular reaction which is possible should really take place. The thought then suggests itself at once that, where reactions which are possible do not take place, there are conditions

existing which were overlooked in the application of the thermodynamical laws and which prevent the reaction from occurring. Such conditions, of which there are indeed indications in many cases, may be comprehensively termed **passive resistances**. They may be capillary actions, perhaps, or mechanical hindrances or friction or something of that sort. These passive resistances may sometimes greatly retard the reaction-velocity, especially at low temperatures. We already saw an example of this in § 12 in a mixture of hydrogen and oxygen. Moreover PICTET has shown that sodium, which reacts rather vigorously with alcohol at ordinary temperatures, floats on it quietly at  $-80^{\circ}$  without any apparent reaction; even concentrated hydrochloric acid and marble do not react upon each other, or at least only very slowly, when they are cooled to a low temperature.

It has been found from thermodynamical laws that the variation of the reaction-velocity with the temperature may in general be expressed thus: when the temperature increases arithmetically, the velocity increases geometrically. Experience has farther shown that a temperature-rise of ten degrees generally involves about a doubling or trebling of the reaction-velocity.

It is not difficult to see what an exceedingly important rôle the passive resistances above referred to play in nature. Were it not for them, the phenomena of combustion, the oxidation of metals, etc., could take place at ordinary temperatures; everything combustible would then burn and there could be no animal and vegetable life on the earth.

## NITROGEN.

**105.** This element occurs free in the air, which contains about 80% nitrogen and 20% oxygen. In combination, it is found in the salts of nitric acid, e.g. saltpetre, and also in the albuminoids, which form an important constituent of animal and vegetable organisms.

Nitrogen can be easily isolated from the air by removing the oxygen. This is accomplished in various ways. Phosphorus, when burned in the air, absorbs the oxygen to form phosphorus pentoxide, and the residual gas, aside from slight admixtures



(§ 110), is nitrogen. Again, air can be passed over heated copper in a finely divided condition, whereupon copper oxide is formed and nitrogen left.

In this process the oxygen of the air soon converts all the copper into copper oxide, so that of course only a limited amount of nitrogen can thus be obtained with the aid of a definite amount of copper. However, if the air is first passed through ammonia water, the process can be carried on continuously, since the hydrogen of the ammonia,  $\text{NH}_3$ , constantly reduces the oxidized copper.

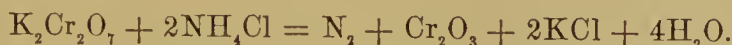
Copper can also absorb the oxygen of the air at ordinary temperatures, if it is treated with a solution of ammonia and ammonium carbonate. Moist phosphorus combines with oxygen even at ordinary temperatures, so that a volume of air which remains in contact with pieces of phosphorus for some minutes loses its oxygen. An alkaline solution of pyrogallol also has the ability to absorb oxygen at ordinary temperatures. These reactions are made use of in gas-analysis.

Pure nitrogen is obtained by the direct decomposition of certain of its compounds, especially by heating ammonium nitrite.

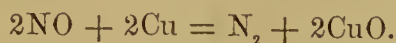


This is usually accomplished by boiling a solution of equal parts by weight of potassium nitrite,  $\text{KNO}_2$ , sal ammoniac,  $\text{NH}_4\text{Cl}$ , and potassium bichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , in 3 parts of water. The  $\text{NH}_4\text{Cl}$  and  $\text{KNO}_2$  react to form  $\text{KCl}$  and  $\text{NH}_4\text{NO}_2$ .

By heating ammonium chromate,  $(\text{NH}_4)_2\text{CrO}_4$  (a mixture of ammonium chloride and potassium bichromate is more convenient), nitrogen is also set free:



An example of the formation of nitrogen by the indirect decomposition of its compounds is the reduction of nitrogen oxides by hot copper:



*Physical Properties.*—Nitrogen is a colorless and tasteless gas. Its specific gravity based on air is 0.97809; its density compared

with hydrogen is therefore 13.998. 1 l. N weighs 1.25749 g. at  $0^{\circ}$  and 760 mm. It is one of the most difficult gases to condense, its critical temperature being  $-146^{\circ}$ . Its boiling-point is  $-194^{\circ}$ . At  $-214^{\circ}$  it becomes solid. It is only slightly soluble in water, even less so than oxygen.

*Chemical Properties.*—Nitrogen is chemically very indifferent; it unites with no element at ordinary temperatures and at higher temperatures with only a few. Boron, silicon, titanium, barium, strontium, calcium, magnesium, chromium and also certain rare elements combine directly with nitrogen at red heat, forming nitrides. Magnesium nitride has the formula  $Mg_3N_2$ . Nitrogen unites with oxygen under the influence of induction sparks directly (reddish brown  $NO_2$  being formed); with hydrogen it combines in a similar way. When a mixture of hydrogen and nitrogen, together with a few drops of concentrated hydrochloric acid, is introduced into a tube over mercury and induction sparks sent through, clouds of ammonium chloride,  $NH_4Cl$ , are produced, the nitrogen and hydrogen having united to form ammonia,  $NH_3$ . These last two reactions and the fact that nitrogen is not able to support combustion serve for the identification of nitrogen gas.

The *molecule of nitrogen* consists of two atoms, as has been demonstrated in the same way as for oxygen and other gaseous elements.

#### THE ATMOSPHERE.

106. The air was regarded as an element up to the end of the eighteenth century. It finally developed from the investigations of PRIESTLEY and LAVOISIER that it is not a simple body. The correct explanation of the phenomena of combustion led to this conclusion.

Before LAVOISIER's time the explanation of the phenomena of combustion was just the reverse of the present one. It was then thought that all combustible or oxidizable substances had a common constituent, **phlogiston**. According to this theory, which was presented by STAHL (1660-1734), the combustion of a body is due to the escape of phlogiston. If this occurs in a violent manner we have the phenomenon of fire. The more inflammable a substance is, the more phlogiston it was supposed to contain. Sulphur, phosphorus, carbon and hydrogen therefore ranked as being very rich in phlogiston. As to the real nature of this phlogiston opinions were decidedly different. At various times experiments were performed with the

hope of isolating the substance. For a while it was thought with CAVENDISH that hydrogen was pure phlogiston.

The prevailing ideas were as follows: Substances that possess much phlogiston can transfer it to those which have none or very little. The metals, for example, are substances that contain a certain amount of phlogiston, which they give off on being heated in the air; by this process they are changed to calxes (now called oxides), which contain no phlogiston. When one of these calxes is heated with carbon or hydrogen, it absorbs phlogiston from them and is changed back again to the metal. The fact that sulphur, phosphorus or any other inflammable substance soon ceases to burn when it is enclosed in an air-tight space was explained by the supposition that the air has then become so saturated with phlogiston that the latter can no longer escape from the burning body.

We see from the above that this theory led men to view many phenomena from a common standpoint and undoubtedly contributed in no small degree to the advancement of chemistry. So long as the phenomena of burning were regarded in that light, there was no occasion to doubt the elemental nature of air. They believed that bodies lose something when they are burned, while we now know that on the contrary something is taken up from the air. The great mistake of the phlogiston theory was, that it did not regard the increase in weight of the burned body; as soon as LAVOISIER and others drew attention to this most important fact, the phlogiston theory could no longer be upheld.

On the first of August, 1774, PRIESTLEY had discovered oxygen, which he himself regarded as air devoid of phlogiston ("dephlogisticated air");<sup>1</sup> LAVOISIER, however, recognized this substance as the essential principle of all burning and oxidization. It now required only a step to reach the conception that air is not an element, but contains another gas in addition to oxygen, and that this gas does not support combustion. The experiment by which LAVOISIER demonstrated this has been already described (§ 9). By measuring the amount of nitrogen which remained after the absorption of the oxygen by hot mercury he was able to determine fairly accurately the composition of air.

*Constituents of the Atmosphere.*—Besides oxygen and nitrogen air contains argon and the other elements described in § 110, hydrogen (0.02%), and also variable amounts of water vapor, carbon dioxide (very nearly 0.04% on the average), ammonia, ozone and perhaps hydrogen peroxide (the last three in extremely small

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<sup>1</sup> From the letters and laboratory notes of SCHEELE, published by Baron NORDENSKIÖLD (Stockholm, 1892), it is evident that oxygen was known to SCHEELE sooner than to PRIESTLEY; he called it "*Feuerluft*." However, this discovery did not seem to lead him any nearer than PRIESTLEY to a correct understanding of the phenomena of burning.

quantities). Incidentally sulphur dioxide and other gases are found in the air (c.g. in the vicinity of volcanoes). The lower strata of air always contain floating dust-particles, microbes, etc.

107. *Analysis of Air.*—The proportional amounts of oxygen and nitrogen in carefully dried air, free from carbon dioxide, etc., has been repeatedly determined with all due precaution. According to the method of DUMAS and BOUSSINGAULT this can be done as follows:

The tube, *ab* (Fig. 42), containing copper turnings is connected with the globe, *V*, all air having been removed from both. The end of the tube marked *b* is attached to the various pieces of apparatus,

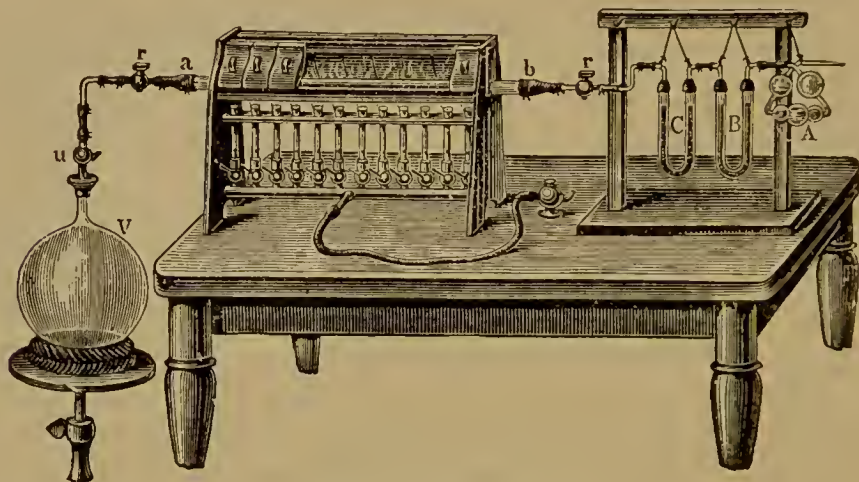


FIG. 42.—ANALYSIS OF AIR.

*C*, *B* and *A*, which are to remove the carbon dioxide and water vapor from the inflowing air. The globe, *V*, is first carefully weighed without air. Thereupon the tube is heated by means of a furnace and a slow current of air is allowed to pass through it to the globe by partially opening the stop-cocks *u* and *r*, the oxygen being meanwhile absorbed by the hot copper. By subsequently weighing the globe the amount of nitrogen which it contains can be determined and by weighing the tube before and after we can find the amount of oxygen. In this way the ratio of oxygen to nitrogen in air can be ascertained.

Another method is the *eudiometric method*. A known volume of air is mixed with a sufficient known volume of pure (electrolytic) hydrogen. On allowing an electric spark to pass through, the hydrogen and oxygen unite to form water, which is deposited

on the sides of the vessel. Inasmuch as 2 vols. hydrogen combine with 1 vol. oxygen, one-third of the volume that disappeared must have been oxygen.

108. These and other methods of investigation have shown that *the composition of the air is nearly constant*. In all parts of the earth, as well as at the highest altitudes which balloons have reached, it consists of

20.81% oxygen and 79.19% nitrogen by volume; and  
23.01% “ “ 76.99% “ “ weight.

The observed variations from this ratio amount to hardly  $\pm 0.1\%$ . Moreover, the composition does not appear to change with time; our present analyses agree with those of DUMAS and BOUSSINGAULT made in 1841.

This result seems surprising at first thought, because oxygen and nitrogen are constantly being removed from the air and again returned to it and it does not necessarily follow, indeed it is rather an improbability, that the losses and gains will exactly balance.

The oxygen passes through the following cycle: Free oxygen is consumed in all sorts of oxidations, particularly in the respiration of animals and plants and in the burning of fuels, carbon dioxide being formed. This carbon dioxide is employed by the plants in their process of assimilation, whereby the oxygen in it is again given back to the air. It will therefore depend on the extensiveness of this process as to whether just as much oxygen gets back into the air as was previously taken up in the formation of carbon dioxide. The oxygen which serves for other oxidations does not necessarily return to the air.

Nitrogen passes through a cycle too. Most of the nitrogen that occurs in the form of organic compounds in animal and vegetable tissues remains in the combined state after the death of the organism, either as ammonia or as nitric acid or in other nitrogenous products. During the process of decay the combined nitrogen is partially liberated; in the burning of plant and animal remains all of it is set free. On the other hand, certain plants, the *Leguminosæ*, are able by symbiosis with bacteria to absorb free nitrogen from the air directly; moreover, in storms some nitrogen combines with oxygen, and again, silent electric discharges, such as must frequently pass between earth and clouds, cause the

nitrogen to enter into combination. Here the question again arises whether as much comes back to the air as goes out.

From what has been said it is sufficiently clear that it would be a mere coincidence if exactly as much oxygen should happen to be withdrawn as is given back. Approximate compensation probably takes place, but, even if it should not, the atmosphere is so vast that its composition would be only slightly affected in the course of centuries.

The following calculation will convince one of the soundness of this argument: The normal atmospheric pressure is 760 mm. mercury; this is due to the weight of the air and the moisture in it. Granted that the pressure of the latter averages 10 mm., we have 750 mm. left for the pressure of the air itself; i.e. the weight of the air is equal to that of a layer of mercury 750 mm. thick extending over the entire surface of the earth. This weight can be calculated thus: The volume of the space between two concentric spheres is  $4\pi R^2r$ , if  $R$  is the radius of the inner sphere, and  $r$  the thickness of that space. The radius of the earth ( $R$ ) is, on the average, 6,370,284 m.;  $r$  is 0.75 m.; therefore, taking into consideration the specific gravity of mercury (13.59), we have for the desired weight of mercury or air  $5.2 \times 10^{18}$  kg. or 5.2 trillion\* kilograms. Since 1 m.<sup>3</sup> air at 0° and 760 mm. pressure weighs 1.2932 kg., the above weight corresponds to a volume of air of  $4 \times 10^{18}$  m.<sup>3</sup> (at 0° and 760 mm.) or  $\frac{4}{5} \times 10^{18} = 8 \times 10^{17}$  m.<sup>3</sup> of oxygen. In comparison with this the amount of oxygen which is withdrawn from the air in breathing, burning, etc., is very small. An adult human being consumes about 600 liters of oxygen every twenty-four hours, or 219,000 liters (219 m.<sup>3</sup>) a year. The population of the earth is not quite  $1500 \times 10^6$ ; all these people therefore require  $328.5 \times 10^9$  m.<sup>3</sup> of oxygen in a year. Assuming farther, which is a very high estimation, that the total consumption of oxygen is ten times the amount required for human respiration, the atmosphere would be deprived each year of  $328.5 \times 10^{10}$  m.<sup>3</sup>, i.e. the  $416 \times 10^{-6}$ th part of the whole amount. The relative insignificance of this amount is better understood when we reflect that 0.1% of all the oxygen on hand would be  $8 \times 10^{14}$  m.<sup>3</sup>. According to the above calculation of the annual need there would be enough oxygen to supply the demand for 244 years without allowing for any compensation. Since, however, the assimilative process of the plants yields a considerable amount in addition, the variations in the proportion of oxygen in the air must obviously be imperceptible with our present analytical methods.

The air is a mixture. It cannot be a compound of nitrogen and oxygen for the following reasons: (1) the ratio of nitrogen to oxygen is different than it would be for a compound of

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\* "Quintillion" in the U. S.—Tr.

the two elements, for in the latter case it would have to correspond to the ratio of the atomic weights or a multiple of the same; (2) by mixing nitrogen and oxygen in the ratio in which they exist in air a synthetical air is obtained which is in every respect like that around us. (This excludes the possibility of air containing a perceptible amount of a compound of the two elements in addition to free nitrogen and free oxygen.) (3) The ratio of the solubilities of the oxygen and the nitrogen of the air in liquids is not the same as that of their occurrence in air; (4) when liquid air boils the first part of the distillate is chiefly nitrogen.

109. The liquefaction of air is now carried on in commerce. The methods used by LINDE and by HAMPSON are based on the same principle, namely, cooling the air by dilatation. Further details may be found in text-books on physics.

Liquid air is very mobile and has a bluish tint. It is usually somewhat cloudy because of suspended particles of ice (congealed atmospheric moisture) and solid carbon dioxide. These may be removed by filtration through filter-paper. It boils at about  $-190^{\circ}$ . It is now extensively used in producing, and demonstrating the effects of, very low temperatures. When carbon dioxide, for example, is led into a flask containing liquid air, it falls in the solid form like snow-flakes. In spite of its low temperature it can be poured upon the hand without danger; it does not even feel cold (on account of the LEYDENFROST phenomenon). Liquid air is much richer in oxygen than the gaseous air of the atmosphere, containing about 50%. If a glowing splinter is dipped into the liquid, the wood begins to burn very vigorously, producing a violent reaction. It can be preserved for a rather long time in vacuum-flasks. Recently liquid air is reported as finding use as an explosive, especially in blasting; unfortunately, however, the cartridges have to be fired within a few minutes after charging.

#### ARGON, HELIUM AND COMPANION ELEMENTS.

110. Argon. Despite the fact that air had been already analyzed times without number, it was first discovered in the course of investigations by RAYLEIGH and RAMSAY in 1894 that there are other elements in the air than nitrogen and oxygen. One of these, named *argon* by its discoverers, is even found to the extent of 0.9% (vol.) or 1.2% (by weight). It was on account of its extraordinary resemblance to nitrogen that it was so long overlooked. The first indication of its presence was the observation that the specific gravity of nitrogen isolated from the air is somewhat higher than that prepared from ammonium nitrite and other compounds. 1 liter of nitrogen from air weighed 1.2572 g., while the same amount from chemical compounds weighed 1.2521g. There must therefore be another gas heavier than nitrogen, mixed in with the nitrogen of the air.

Two methods were employed by the investigators above named to isolate this gas. The first one was to pass the air first over hot copper in order to remove the oxygen, and then over red-hot magnesium, which absorbs the nitrogen (§ 107). There still remained a small quantity of gas which was not nitrogen. The other method was to submit a mixture of air and oxygen over caustic potash to the action of induction sparks for a long time. The oxygen thus combines with the nitrogen, forming compounds which are absorbed by the potash. At the end the excess of oxygen is removed by some absorbing-agent (§ 105). In this case also there is a remainder of gas. Still other methods have been devised for obtaining argon from the air. One of the simplest is to heat air with a mixture of 1 g. magnesium, 0.25 g. sodium and 5 gr. freshly ignited lime. On account of the high temperature free calcium is formed



and it is in such a finely divided condition that it absorbs oxygen greedily and also nitrogen, so that only argon is left.

After argon had been once discovered it was also found elsewhere than in the atmosphere; some mineral waters contain it in solution, certain rare minerals yield it when heated, etc.

Argon is a colorless odorless gas, having a specific gravity of 19.957. Its molecular weight is therefore 40. It has been found (page 167) that the molecule consists of only one atom and that the atomic weight is therefore 40 ( $O = 16$ ) too. It has been condensed to a colorless liquid, that boils at  $-186.9^\circ$ , by cooling with boiling oxygen and compressing it to about 50.6 atmospheres; it solidifies at  $-189.6^\circ$ . It is somewhat more soluble in water than is nitrogen (0.05780 parts in 1 vol. at  $0^\circ$  and 760 mm. pressure). As to its chemical nature, it is interesting that as yet no compounds of argon have been able to be prepared.

It is certain that what is now called argon is neither a mixture nor a compound, but an element. The boiling-point and the melting-point are constant, and the vapor-pressure of argon likewise remains constant during the liquefaction, so long as any gas is present. Moreover, when a certain volume of argon is three-fourths dissolved in water, the undissolved gas shows exactly the same spectrum as the dissolved. All of the above are characteristics of a homogeneous substance. The extraordinary stability of the gas in the presence of all sorts of reagents is a strong argument against its being a compound.

After the discovery of argon, RAMSAY detected four other rare gases in the atmosphere, though their quantity is very small. These are *helium*, *neon*, *krypton*, and *xenon*. Helium obtained its name because its existence on the sun (§ 267) had already been pointed out before it was discovered on the earth. In 1895 RAMSAY succeeded, however, in obtaining it in small amounts on heating the rare mineral *cleveite*. Afterward it was



also met with as a companion of argon in certain other, chiefly uraniferous, minerals as well as in mineral springs. When air is liquefied, a part of it always escapes condensation; this part consists chiefly of nitrogen, but contains also helium and neon. Nitrogen can be removed from this mixture by the methods already described above (p. 160). When the resulting mixture of helium and neon is then cooled with boiling hydrogen, neon alone is condensed.

At ordinary temperatures helium is a colorless gas. It has been liquefied; its boiling-point is very low, somewhere near that of hydrogen. It is less soluble in water than argon. As to its elemental nature, there is no occasion for doubt; it could not be separated into two parts by diffusion. So far no compounds of helium are known.

While helium and neon were found in the most volatile part of the air, krypton and xenon were obtained, on the contrary, from the residue, after a large quantity of liquid air had been allowed to evaporate slowly. Their separation was rendered possible by the fact that krypton still has a rather large vapor-tension at the temperature of liquid air, while the vapor-tension of xenon is then imperceptible.

Both these elements occur only in extremely small amounts in the atmosphere. The proportion is about as great as that of gold in sea-water. RAMSAY found 4 c.c. xenon in 600,000 l. air.

In the following table some of the constants of these elements are given.

	Helium.	Neon.	Argon.	Krypton.	Xenon.
Density (O = 16) . . . .	1.98	9.97	19.96	40.88	64
Atomic weight . . . . .	4	20	40	81.7	128
Boiling-point at 760 mm. . . . .			86.9° abs.	121.33° abs.	163.9° abs.

These gases have two other properties in common which are worthy of mention here. In the first place, they display characteristic spectral lines in Plücker tubes (§ 263) whereby it has been possible to recognize them and to judge of their purity.

In the second place, they possess the property already alluded to in the case of argon, whereby their molecule consists of only one atom. This fact could not be discovered in the ordinary way, described in §§ 33 and 34, because none of these elements are able to form compounds with others; their valence can be said to be zero. It has, however, been possible to ascertain it from the *molecular heat* of the gases. This is the amount of heat that must be imparted to a gram-molecule of a gas in order to raise its temperature one degree. For gases with two atoms in their molecule the molecular heat is about 5 Cal.; with 3 atoms about 7.5 Cal.; but for mercury, whose molecule has only one atom (as can be proved according

to §§ 33 and 34) it is only 2.5. Now, since the density of argon is found to be nearly 20 ( $H = 1$ ), its molecular weight is 40. For this weight the molecular heat was found to be about 2.5, which proves that argon has only one atom in its molecule, and that the latter therefore weighs 40. In the same way similar results have been obtained for the other rare gases of the atmosphere.

### Compounds of Nitrogen and Hydrogen.

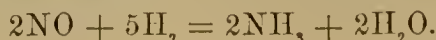
111. Until recent years only one compound of hydrogen and nitrogen has been known, viz., *ammonia*,  $NH_3$ . At present, however, we know of five: the others being *hydrazine*,  $N_2H_4$ , *hydrazoic acid*,  $N_3H$ , and the *compounds of the latter with ammonia and with hydrazine* ( $NH_3 \cdot N_3H$  and  $N_2H_4 \cdot N_3H$ ). Of these five compounds, however, ammonia is by far the most important.

#### AMMONIA.

The material now used for obtaining ammonia is the "ammonia liquor" of the gas-factories. The gases that are given off in the dry distillation of coal are passed through water, which dissolves the ammonia.

In order to obtain a pure ammonia, the ammonia liquor is heated with milk of lime and the expelled ammonia is led into concentrated sulphuric acid. In this way crystallized ammonium sulphate is obtained. It is purified by recrystallization and again distilled with lime to recover the free ammonia.

Ammonia can be prepared synthetically by the following methods, which are as yet, however, without any industrial importance. The direct synthesis from the elements was given above (§ 107). There are also examples of its formation by the direct decomposition of its compounds. Thus we obtain it by heating the ammonia compounds of certain salts, as  $xCaCl_2 \cdot yNH_3$  and  $xAgCl \cdot yNH_3$ . A number of organic compounds yield nitrogen in the form of ammonia on heating. Moreover, ammonia results from the action of hydrogen on certain nitrogen compounds, as, for example, when nitric acid,  $HNO_3$ , comes in contact with nascent hydrogen (generated from zinc or iron-filings and dilute sulphuric acid), or when a mixture of nitric oxide,  $NO$ , with hydrogen is passed over platinum black:



The formation of ammonia by the action of free nitrogen on hydrogen compounds has not been brought about, but the gas can be produced by the interaction of a hydrogen compound with a nitrogen compound. An illustration of this is the decomposition of magnesium nitride (§ 107) by water:



The putrefaction of organic matter (fæces, urine, etc.) evolves ammonia. By the action of electric sparks on moist air ammonium nitrate is produced. These last two methods of formation are responsible for the slight traces of ammonia in the air.

*Physical Properties.*—Ammonia at ordinary temperatures is a gas with a characteristic odor, that excites one to tears. Its specific gravity is 8.5 ( $H = 1$ ) or 0.589 (air = 1); 1 l.  $\text{NH}_3$  at  $0^\circ$  and 760 mm. pressure weighs 0.76193 g. It can be easily liquefied; it boils at  $-33.7^\circ$  and becomes solid at  $-75^\circ$ ; it then forms

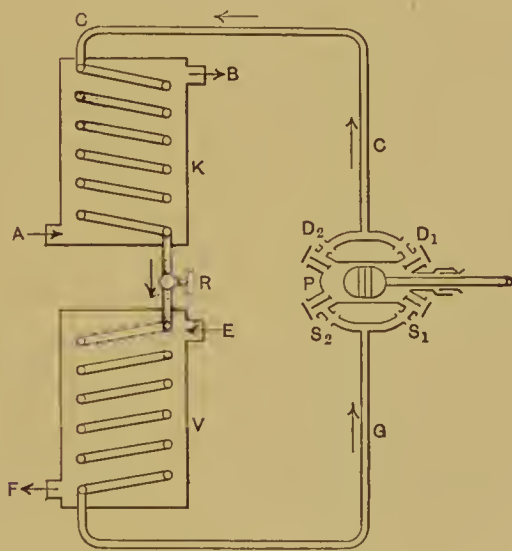


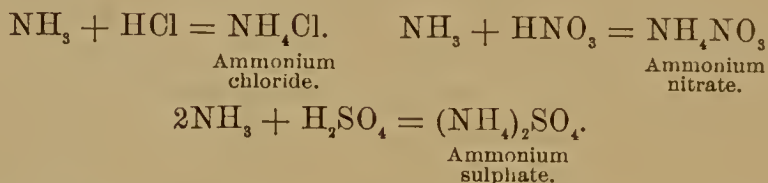
FIG. 43.—DIAGRAM OF AN ICE-MACHINE.

white translucent crystals. It is extremely soluble in water; at  $0^\circ$  and normal pressure 1 vol.  $\text{H}_2\text{O}$  dissolves 1148 vols., or 0.875 parts by weight, of  $\text{NH}_3$ . The specific gravity of the solution of ammonia in water grows smaller as the concentration increases.

The evaporation of liquid ammonia involves a considerable depression of temperature. This is the principle of most of the ice-machines now in use. They consist mainly of two serpentes  $K$  and  $V$  (Fig. 43); the first is plunged in a vessel through which cold water flows; the second contains a concen-

trated salt solution. *P* is a pump, which draws ammonia gas through *G* by means of the valves *S*<sub>1</sub>*S*<sub>2</sub> and which compresses the gas through *G'* by means of the valves *D*<sub>1</sub> and *D*<sub>2</sub>. The gas thus liquefied in *K* is allowed to enter *V* through the cock *R*. There it evaporates quickly and so cools the salt solution below 0°. If a vessel of water be plunged into the salt solution the water will be frozen in a short time. The machine thus works continuously.

*Chemical Properties.*—The characteristic property of this compound is that *it combines with acids directly to form salts* :

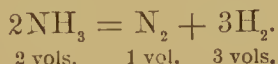


In these salts (which are almost all readily soluble in water) the atomic group  $\text{NH}_4$  plays the part of a metal; they correspond in every respect to the compounds  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ , etc. The group, or radical,  $\text{NH}_4$  has been given a particular name; it is called **ammonium**. More than one attempt has been made to isolate this ammonium, but always in vain. However, when sodium amalgam comes in contact with a concentrated ammonium chloride solution, the mercury swells to a soft spongy mass that rapidly decomposes at ordinary temperatures into ammonia and hydrogen and is in all probability therefore ammonium amalgam.

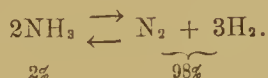
The aqueous solution of ammonia reacts strongly basic; so do the moist fumes of ammonia. We must therefore assume that this solution contains a compound  $\text{NH}_4\text{OH}$ , ammonium hydroxide, and hence also the ions  $\text{NH}_4$  and  $\text{OH}$  in analogy with other soluble bases, e.g. potassium hydroxide,  $\text{KOH}$ . This supposition is also confirmed by the fact that this solution conducts electricity, although not nearly so well as a potassium hydroxide or sodium hydroxide solution of the same value (§ 234). The isolation of ammonium hydroxide has, however, not yet been accomplished: on evaporating its solution it breaks up into  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . Ammonia can be completely expelled from aqueous solutions by boiling.

Ammonia does not burn in the air but does in oxygen; in addition to water and nitrogen traces of ammonium nitrite,  $\text{NH}_4\text{NO}_2$ , and nitrogen dioxide,  $\text{NO}_2$ , are also formed. A mixture of

ammonia and oxygen explodes violently when it is ignited. The oxygen conveyed by soil-bacteria may also cause the oxidation of ammonia, producing nitric acid. Chlorine takes fire when passed into ammonia, forming nitrogen,  $N_2$ , and hydrochloric acid; the latter then unites with the remaining ammonia to form sal ammoniac,  $NH_4Cl$ . The hydrogen of ammonia is replaceable by metals. Magnesium, e.g. burns in ammonia, forming magnesium nitride,  $Mg_3N_2$ . When ammonia is conducted over hot potassium or sodium, potassium amide,  $NH_2K$ , or sodium amide,  $NH_2Na$ , is formed. These and analogous metal compounds are decomposed by water, yielding ammonia again and also metal oxide or hydroxide. At high temperatures (produced by induction sparks) ammonia splits up almost completely into its elements, the volume being doubled:



112 On the other hand, nitrogen and hydrogen can unite to form ammonia under the influence of induction sparks (§ 107). Equilibrium is reached when 2% of ammonia is formed. This the reason why ammonia cannot be split up by electric sparks to more than 98%:



Nevertheless  $N_2 + 3H_2$  can be completely converted into  $NH_3$  by induction sparks when these gases are in contact with an acid; in this way ammonia is constantly withdrawn from the gaseous system  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ; the remaining gas mixture will therefore form new  $NH_3$  in order to restore the equilibrium, and so on, until all the nitrogen and hydrogen have combined.

113. *Composition of Ammonia.*—If an aqueous ammonia-solution (to which has been added a little sodium chloride to aid conduction) is subjected to electrolysis, nitrogen and hydrogen are generated in the volume-ratio of 1 : 3; from this it follows that the molecule must contain 3 H-atoms to every 1 N-atom, i.e. the empirical formula is  $NH_3$ . Since the specific gravity of ammonia gas is 8.5 ( $O = 16$ ), the molecular weight is 17, which corresponds to the above formula.

HYDRAZINE, DIAMIDE,  $N_2H_4$ .

114. This compound can be obtained by the action of sulphurous acid on potassium nitrite, which yields a compound  $K_2SO_3N_2O_2$ , nitrosylpotassium sulphite. When the latter is reduced in aqueous solution by sodium amalgam, hydrazine is formed:



It is far easier to prepare hydrazine from some organic substances, but these methods fall outside of the scope of this book.

By fractional distillation of the aqueous solution the hydrate  $N_2H_4 \cdot H_2O$  is obtained, which boils constant at  $118.5^\circ$ ; it is a liquid at ordinary temperatures and freezes below  $-40^\circ$ .

LOBRY DE BRUYN showed that the molecule of water can be removed by treatment with barium oxide and the *free hydrazine* obtained in the pure state by distillation under reduced pressure. This substance is liquid at ordinary temperatures, congeals at  $1.4^\circ$  and boils under ordinary pressure at  $113.5^\circ$ . Sp. g. = 1.014 at  $15^\circ$ . It unites with water to form the above hydrate with the evolution of heat. Both the free hydrazine and its aqueous solution have a strong reducing action. The former gradually oxidizes in the air, reacts vigorously with the halogens, etc. The aqueous solution precipitates the metals from solutions of salts of copper, mercury, silver, etc., at ordinary temperatures.

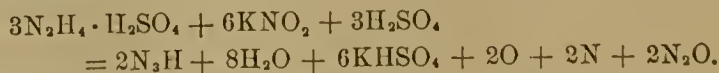
Hydrazine, like ammonia, unites with acids directly to form salts; it can take up either one or two molecules of a monobasic acid,  $N_2H_4 \cdot HCl$  and  $N_2H_4 \cdot 2HCl$  being both known. The hydrate is probably therefore the *hydrazonium hydroxide*,  $NH_2 \cdot NH_3OH$ ; the aqueous solution is strongly basic. The salts of hydrazine are easily soluble in water, excepting the sulphate,  $N_2H_4 \cdot H_2SO_4$ , which is rather difficultly so.

HYDRAZOIC ACID,  $N_3H$ .

115. This interesting compound, like the preceding one, was first discovered by CURTIUS as a product of organic compounds. It can be prepared by a purely inorganic method, viz. by passing nitrous oxide over sodium amide,  $NaNH_2$ , at a high temperature (§ 111),



or by treating hydrazine sulphate (§ 114) with nitrous acid:



An aqueous solution of the free acid is best obtained by distilling lead

hydrazoate  $Pb(N_3)_2$ , with dilute sulphuric acid. By fractional distillation of this solution, the pure acid can be obtained.

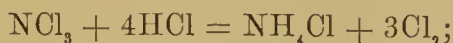
Pure hydrazoic acid is a liquid with a penetrating unbearably odor; it boils at  $37^\circ$  and is extremely explosive, even in aqueous solution.

It is a strange fact that hydrazoic acid displays more or less analogy with the hydrogen acids of the halogens; it forms, like them, difficultly soluble salts of silver, mercury (ous) and lead. These are, however, soluble in strong mineral acids. They are also very explosive, hence extremely dangerous, the sodium salt being the least so. An aqueous 1% solution of the acid is only 0.008 ionized; it is thus a rather weak acid; it gives off hydrogen in contact with many metals, e.g. Zn, Fe, Cd and Mg. It is especially characteristic of the metal-azides that they all crystallize anhydrous and always yield the pure metal when heated.

### Compounds of Nitrogen with the Halogens.

116. When chlorine gas is allowed to act on a concentrated solution of ammonium chloride, most conveniently by inverting a flask full of chlorine over the warm ( $30^\circ$ – $40^\circ$ ) solution, oily drops are formed, which are best collected in a leaden saucer placed under the mouth of the flask. These drops contain some hydrogen as well as nitrogen and chlorine. By treating with chlorine once more pure **nitrogen trichloride**,  $NCl_3$ , is obtained as a yellowish oil with a disagreeable pungent odor and a specific gravity of 1.65. This is one of the most dangerous of substances, because it explodes in a most violent manner, not only on contact with certain organic substances (e.g. turpentine), but very often spontaneously. It dissolves in carbon bisulphide, benzene and other solvents, forming yellow solutions. These solutions are relatively harmless; they decompose in the sunlight.

Concentrated hydrochloric acid decomposes nitrogen trichloride according to the equation:



aqueous ammonia also breaks it up in a similar way:



Nitrogen trichloride is strongly endothermic:

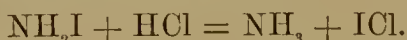


**117. Nitrogen Iodide.**—Various compounds are known which consist of nitrogen, iodine and hydrogen; the one or the other is obtained according to the manner of treating iodine with ammonia. If a solution of iodine in potassium iodide is mixed with ammonia solution, a precipitate is usually obtained of the composition  $\text{NI}_2\text{H}$ ; if the conditions are slightly altered another compound,  $\text{N}_2\text{I}_3\text{H}_3$  (i.e.  $\text{NH}_3 + \text{NI}_3$ ), is deposited, which breaks up on continued treatment with water into ammonia and  $\text{NI}_3$ . These compounds are likewise very explosive.

Another method is to digest pulverized iodine with ammonia water. The product so obtained is still more explosive, often exploding even when damp or when it is being washed with water or by the action of hydrochloric acid. In the presence of ammonia solution it is stable.

When liquid ammonia is treated with iodine between  $-80^\circ$  and  $-30^\circ$ , compounds of ammonium tri-iodide with several molecules of ammonia are obtained; they gradually part with a small amount of ammonia.

Nitrogen iodide is decomposed by dilute hydrochloric acid, forming ammonia and chlorine iodide:



Nitrogen iodide is also decidedly endothermic.

### Hydroxylamine, $\text{NH}_2\text{OH}$ .

**118.** Hydroxylamine is a reduction product of many oxygen compounds of nitrogen intermediate to the formation of ammonia; e.g. it is formed when tin acts on dilute nitric acid. Here the nascent hydrogen effects the reduction:



LOBRY DE BRUYN succeeded in preparing hydroxylamine in the pure anhydrous condition. He added sodium methylate to a solution of the hydrochloride in absolute (i.e. anhydrous) methyl alcohol, by which a solution of free hydroxylamine in the latter is obtained. This solution is freed from the precipitated sodium chloride by filtration and then the alcohol is removed by distillation, at first under ordinary pressure; the free base  $\text{NH}_2\text{OH}$  is then obtained pure by fractionating under diminished pressure. It is a crystalline solid, melting at  $30^\circ$  and boiling at  $70^\circ$  under 60 mm. pressure. When heated in the air, it explodes with a yellow flame.



Hydroxylamine is easily soluble in water; its solution reacts strongly alkaline. It forms salts in the same way as ammonia, i.e. by direct addition of the acid:  $\text{NH}_2\text{OH} \cdot \text{HCl}$ ,  $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ , etc. These salts are rather stable; the hydrochloride must be preserved over lime, else it slowly decomposes. The salt is namely split up to a very small degree into hydrochloric acid and hydroxylamine. Now free hydrochloric acid accelerates catalytically the decomposition of the salt. When, however, the hydrochloric acid is absorbed by the lime, the decomposition becomes so slow that it is imperceptible. The free hydroxylamine and its aqueous solution are somewhat unstable, especially in the presence of alkalies; it decomposes easily into ammonia, water and nitrogen.

A farther characteristic of hydroxylamine is its great reducing power; it precipitates reddish-yellow cuprous oxide from an alkaline copper solution at ordinary temperatures, even when strongly diluted; mercuric chloride,  $\text{HgCl}_2$ , is reduced to calomel,  $\text{HgCl}$ ; silver nitrate to silver, etc.

The following reaction is also peculiar: A solution of ferrous sulphate is precipitated with an excess of sodium hydrate and warmed; if hydroxylamine (or one of its salts) is now added to the green ferrous hydrate, red ferric hydrate is formed very quickly, the hydroxylamine being reduced in this alkaline solution to ammonia. On acidifying, an acidic solution of a ferric salt is obtained; if this is treated with a hydroxylamine salt, it is suddenly decolorized because of reduction to ferrous salt, the hydroxylamine being now in the oxidized condition in the acid solution.

### Compounds of Nitrogen with Oxygen.

Those included under this title are: *nitrous oxide*,  $\text{N}_2\text{O}$ ; *nitric oxide*,  $\text{NO}$ ; *nitrogen trioxide*, or nitrous anhydride,  $\text{N}_2\text{O}_3$ ; *nitrogen dioxide*,  $\text{NO}_2$ , or *tetroxide*,  $\text{N}_2\text{O}_4$ , and *nitrogen pentoxide*, or nitric anhydride,  $\text{N}_2\text{O}_5$ .

#### NITROUS OXIDE, $\text{N}_2\text{O}$ .

119. This compound cannot be obtained directly from its elements; the ordinary method of preparation consists in heating ammonium nitrate to about  $250^\circ$ :



This method is analogous to that of preparing nitrogen from

ammonium nitrite (§ 105). If the nitrate is heated above  $250^{\circ}$ , the gaseous product partially decomposes.

*Physical Properties.*—Nitrous oxide is a colorless and odorless gas, which when liquefied boils at  $-87^{\circ}$  and solidifies at  $-102^{\circ}$ . The evaporation of the liquid produces a great depression of temperature that may even reach  $-140^{\circ}$  under reduced pressure. Its specific gravity is 1.52 (based on air), or 21.89 for  $H = 1$ . 1 l.  $N_2O$  at  $0^{\circ}$  and 760 mm. pressure weighs 1.9657 g. It is rather soluble in water (1 vol.  $H_2O$  dissolves 1.305 vol.  $N_2O$  at  $0^{\circ}$ ); hence it must be collected over hot water. In alcohol it is still more soluble.

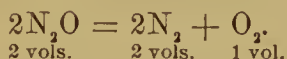
*Chemical Properties.*—Nitrous oxide can support combustion. Phosphorus, carbon and a glowing splinter burn in it as in oxygen. A mixture of nitrous oxide and hydrogen explodes like detonating gas when it is ignited, only not quite so loud. These properties might lead one to confuse it with oxygen on a superficial examination. It is very easily distinguished from the latter by the fact that it gives no red fumes when mixed with nitric oxide (§ 120) and always leaves residual gas (nitrogen) after a combustion. A faintly burning piece of sulphur is moreover extinguished by nitrous oxide.

Nitrous oxide is endothermic:  $2N + O - N_2O = -17.7$  Cal.

BERTHELOT has made the general observation that endothermic substances can suffer an explosive decomposition; in this case this may be brought about by touching off the gas with fulminating mercury. It is easy to explain BERTHELOT'S observation. When an endothermic substance decomposes, heat is evolved. Now, we saw in § 12 that chemical reactions are accelerated in a very high degree by rise of temperature. Suppose that a sudden decomposition is caused at a certain point in a mass of an endothermic compound. The surrounding molecules are heated thereby and they too split up suddenly, thus evolving still more heat, and so on. The whole mass will thus reach a condition of sudden decomposition, that is, it will explode. To bring this about it is only necessary that the first impulse be vigorous enough for the sudden decomposition of so many molecules that the heat evolved is sufficient to raise the surrounding ones to the temperature of decomposition.

The *composition* of nitrous oxide can be determined by mixing

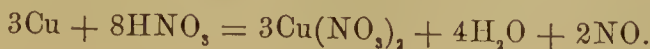
the gas with hydrogen and exploding the mixture. Starting with 100 c.c.  $N_2O$  mixed with 150 c.c. hydrogen, we have remaining after the explosion 150 c.c. of a mixture of nitrogen and hydrogen. In order to determine the amount of hydrogen present we add to the mixture 50 c.c. oxygen and again send a spark through it. We find that the volume is reduced by the explosion from 200 c.c. to 125 c.c.; the contraction was therefore 75 c.c. Of this 75 c.c. two-thirds was hydrogen, so that in the 150 c.c. which remained after the first explosion there was  $150 - 50 = 100$  c.c. nitrogen. Hence 100 c.c. nitrous oxide has yielded 100 c.c. nitrogen. To find the volume of oxygen which was in combination with the nitrogen we must know the amount of hydrogen that disappeared in the explosion. Of the 150 c.c. that was added originally 50 c.c. was left; therefore 100 c.c. hydrogen was consumed in forming water with the oxygen of the nitrous oxide, an amount which requires 50 c.c. oxygen. We thus reach the conclusion that 1 vol. nitrous oxide in decomposing yields 1 vol. nitrogen and  $\frac{1}{2}$  vol. oxygen; this is expressed by the formula  $N_2O$ :



Under the protracted action of induction sparks the gas splits up into a mixture of nitrogen and oxygen, the volume of which is half again as great as that of the nitrous oxide. When potassium and sodium are burned in the gas, potassium and sodium oxides respectively are formed, together with nitrogen; the gas-volume after cooling is unchanged. Both of these observations point to the same formula,  $N_2O$ , as does also the fact that its specific gravity, which should theoretically be  $\frac{2 \times 14 + 16}{2} = 22$  ( $H = 1$ ), was found to be 21.89.

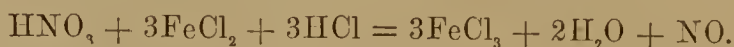
#### NITRIC OXIDE, $NO$ .

120. This gas is only obtained by the reduction of nitric or nitrous acid. The ordinary method of preparation is by allowing copper to act on nitric acid or else by covering copper (in the form of thin sheets) with a saturated solution of saltpetre and adding concentrated sulphuric acid drop by drop (§ 127):



In this reaction the hydrogen, which would be expected to be generated from the nitric acid, reduces another portion of the acid.

In order to prepare nitric oxide by the reduction of nitric acid or a nitrate a boiling-hot solution of ferrous chloride,  $\text{FeCl}_2$ , in hydrochloric acid is found very satisfactory; the ferrous chloride is converted into the ferric chloride,  $\text{FeCl}_3$ , by the reaction:



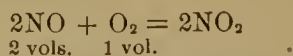
Perfectly pure nitric oxide is obtained by treating a mixture of yellow prussiate of potash and potassium nitrite with acetic acid:



*Physical Properties.*—Nitric oxide is a colorless gas, whose specific gravity has been found to be 1.039 (air = 1). It can be condensed to a liquid, which boils under ordinary pressure at  $-153.6^\circ$ . The critical temperature is  $-93.5^\circ$ , the critical pressure 71.2 atm. It is not very soluble in water, but dissolves easily in a solution of ferrous sulphate,  $\text{FeSO}_4$ ; strange to say, this solution is quite dark brown in color, although the ferrous salt solution is pale green and nitric oxide colorless.

*Chemical Properties.*—It is characteristic of this gas, above all other properties, that it combines with oxygen at once, forming nitrogen dioxide, a reddish-brown gas.

PRIESTLEY, at the end of the eighteenth century, made use of this reaction to determine the proportion of oxygen in the air. To this end he mixed 1 vol. air with 1 vol. nitric oxide and absorbed the red  $\text{NO}_2$  fumes, that were formed, with caustic potash. From the equation:



it follows that one-third of the volume that disappeared was oxygen.

At red heat nitric oxide is converted into dioxide and nitrogen. On heating it with hydrogen no explosion occurs; the mixture burns with a white flame, forming water and nitrogen. If burning phosphorus is introduced into the gas, it continues to burn; a lighted candle is, however, extinguished; sulphur and charcoal do

not burn in it either. A mixture of nitric oxide and carbon bisulphide burns with an intensely luminous blue flame, that is very rich in chemically effective rays.

Nitric oxide is a strongly endothermic compound; it can be made to explode by fulminating mercury.

*Composition.*—When sodium is heated in a measured amount of nitric oxide, sodium oxide and nitrogen are formed; the latter takes up exactly half the volume of the original gas. The specific gravity of nitric oxide is 15 ( $H = 1$ ), hence its molecular weight is 30. According to the above decomposition the gas contains one atom of nitrogen (14 parts by weight). There remain for the oxygen, therefore, 16 parts by weight, i.e. just one atom. Hence the formula is NO.

Since nitrogen is trivalent or quinquivalent (the latter in ammonium salts, e.g.  $NH_4Cl$ ) and oxygen is bivalent, it must be assumed that there is a free valence bond in NO, i.e.  $-N = O$ . The same applies to  $NO_2$ . Free bonds like these are very rare.

#### Nitrous Anhydride, $N_2O_3$ .

121. This compound is only known at low temperatures. It is obtained as a blue liquid when nitric oxide is led into the liquid tetroxide,  $N_2O_4$ , at  $-21^\circ$ . In the gaseous state the compound dissociates completely, even at a low temperature, into  $NO_2$  and NO, as is shown by the vapor density; neither do  $NO_2$  and NO, when mixed in the gaseous condition, give evidence of any contraction, which would necessarily be the case if they united to form  $N_2O_3$ . By the action of arsenious anhydride,  $As_2O_3$ , on nitric acid (sp.g. 1.3) a gas mixture is formed which has almost exactly the composition  $N_2O_3$ , i.e.  $NO_2 + NO$ .

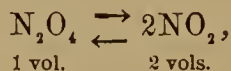
#### NITROGEN DIOXIDE AND TETROXIDE, $NO_2$ AND $N_2O_4$ .

122. Nitrogen dioxide is formed from nitric oxide plus oxygen, or more conveniently by heating well-dried lead nitrate:



When so prepared it is a very deep-brown gas. On leading it into a strongly cooled vessel it condenses to a bright yellow liquid, which solidifies at  $-20^\circ$  to colorless crystals, that melt at  $-12^\circ$ . The color becomes darker on warming and at  $+26^\circ$  the liquid begins to boil, changing back again into the brown gas. The

vapor density of this gas at  $26^\circ$  is found to be 38.0, while that calculated for  $N_2O_4$  is 45.9 and that for  $NO_2$  22.9 ( $H = 1$ ). Since the value found is between the two, it may be assumed that at this temperature the vapor consists partly of  $N_2O_4$  molecules and partly of  $NO_2$  molecules. A simple calculation indicates the percentage of the former to be 34.4%. As the temperature rises, the vapor density steadily decreases till about  $150^\circ$  is reached, when it is constant at 22.9. There is evidently complete dissociation of  $N_2O_4$  molecules in this case,



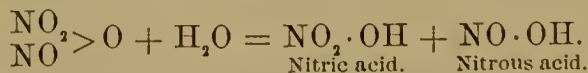
and, inasmuch as the color of the gas grows darker, we must suppose that  $NO_2$  is dark brown, while  $N_2O_4$  is colorless, which is true of the latter in the solid state. This supposition is supported by the fact that the degree of dissociation can not only be estimated from the intensity of the color, but that it can be even measured quantitatively in this way.

According to § 51 the equilibrium between the two gases is expressed by the equation:

$$P - x = kx^2,$$

where  $P$  is the total pressure of the gas mixture and  $x$  that of the dioxide,  $k$  being a constant. From this equation it follows that the dissociation (at a constant temperature) depends on the pressure (§ 51), which has been shown to be the case. This also follows from the theorem of LE CHATELIER (§ 102).

On bringing nitrogen tetroxide in contact with water or, better, with alkalies, nitrous and nitric acids are formed; we may therefore consider it as a mixed anhydride of these two acids:



Both  $NO_2$  and  $N_2O_4$  possess strong oxidizing ability; many substances burn in their vapor; they precipitate iodine from soluble iodides.

The composition of nitrogen dioxide follows from its synthesis-equation,  $2NO + O_2$ , and from the vapor density.

**Nitrogen Pentoxide, N<sub>2</sub>O<sub>5</sub>.**

123. This compound can be obtained by the action of chlorine on silver nitrate or by distilling fuming nitric acid with phosphorus pentoxide. It is a colorless crystalline solid. It melts at 30°, and at 45–50° breaks up, giving off brown fumes. If the heating takes place rather rapidly the decomposition is explosive in nature; sometimes a spontaneous explosion even takes place, hence it can not be kept long.

As nitrogen pentoxide is strongly endothermic, its spontaneous explosion must be explained in the same way as is indicated in § 119. Only we must admit in this case that the decomposition at ordinary temperatures is great enough to sufficiently heat the neighboring molecules.

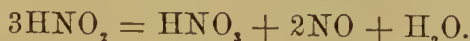
It unites with water, forming nitric acid with the evolution of much heat. As might be expected, it has strongly oxidizing properties. Phosphorus and potassium, for instance, burn with great brilliance in the slightly warmed anhydride.

The composition of nitrogen pentoxide is ascertained by heating with powdered copper; the amount of nitrogen evolved corresponds to the formula N<sub>2</sub>O<sub>5</sub>.

**Oxygen Acids of Nitrogen.**

124. Three acids of nitrogen are known: *hyponitrous acid*, H<sub>2</sub>N<sub>2</sub>O<sub>2</sub>; *nitrous acid*, HNO<sub>2</sub>; *nitric acid*, HNO<sub>3</sub>. The nitrous acid is known only in dilute aqueous solution, but both of the others in the pure state as well.

Only certain ones of the above nitrogen oxides can be regarded as acid anhydrides. The pentoxide is undoubtedly one and the tetroxide may be considered as a mixed anhydride of nitric and nitrous acids (§ 122). Nitrogen trioxide gives a solution of nitrous acid when mixed with water at a low temperature; however, this solution undergoes a decomposition slowly at ordinary, more rapidly at higher, temperatures, nitric acid and nitric oxide being formed:



No acid corresponding to nitric oxide, NO, is known, and also none to nitrous oxide, N<sub>2</sub>O, although hyponitrous acid has the formula N<sub>2</sub>O + H<sub>2</sub>O = H<sub>2</sub>N<sub>2</sub>O<sub>2</sub> and can also really yield nitrous oxide. However, no one has yet been able to obtain hyponitrous acid from nitrous oxide and water.

**Hyponitrous Acid,  $H_2N_2O_2$ .**

125. This acid is formed when nitrogen trioxide is introduced into a methyl-alcoholic solution of hydroxylamine. After neutralization the difficultly soluble yellow silver hyponitrite,  $Ag_2N_2O_2$ , can be precipitated from the solution by silver nitrate. From this salt the free acid is obtained by treating it with ether saturated with hydrochloric acid gas and evaporating the ether, whereupon it is left in the form of white flaky crystals. These are very explosive, and dissolve very easily in water. The freezing-point depression of the aqueous solution shows that the molecular formula is  $H_2N_2O_2$ . On warming the aqueous solution the acid breaks up almost wholly into nitrous oxide and water. When the acid is set free (by the addition of an excess of silver hyponitrite to cold dilute hydrochloric acid) it does not liberate iodine from potassium iodide at once; the reaction is delayed for a time, probably on account of a decomposition, by which nitrous acid is formed.

Hyponitrous acid belongs to the class of weak acids; its aqueous solution is a poor conductor. Both neutral and acid salts of this acid are known.

**NITROUS ACID,  $HNO_2$ .**

126. It was remarked above that this acid is only known in dilute solution at ordinary or low temperatures; its salts are, however, stable. In order to prepare them we usually employ potassium or sodium nitrate, which gives off oxygen when heated and is converted into nitrite. This decomposition takes place more readily if lead is added during the heating as a reducing agent:



Its salts are all easily soluble in water, with the exception of silver nitrite,  $AgNO_2$ , which is rather difficultly soluble at ordinary temperatures; it is obtained as a yellow crystalline precipitate, when not too dilute solutions of silver nitrate are mixed with a nitrite.

The addition of strong sulphuric acid to a nitrite at once produces red fumes; in this way a nitrite can be distinguished from a nitrate, for the latter does not produce them. It may be assumed that in this reaction free nitrous acid is primarily formed: this is, however, broken up directly into water and nitrogen trioxide, the latter of which at once splits up again into  $NO_2 + NO$ : thereupon the nitric oxide unites immediately with the surrounding oxygen to form dioxide. The red fumes thus consist solely of nitrogen dioxide,  $NO_2$ .



On treating a very dilute nitrite solution with the equivalent amount of sulphuric acid a dilute solution of free nitrous acid is obtained. This solution can act either oxidizing or reducing. As examples of the former action we have the liberation of iodine from a solution of potassium iodide, the oxidation of sulphurous acid in dilute solution to sulphuric acid, the oxidation of ferrous sulphate,  $\text{FeSO}_4$ , to ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , and the conversion of the yellow to the red prussiate of potash. In all of these cases lower oxides of nitrogen, chiefly nitric oxide, are formed. An example of its reducing action (in which nitrous acid is oxidized to nitric acid) is the bleaching of potassium permanganate,  $\text{KMnO}_4$ , in sulphuric acid solution:



This last reaction offers a means of determining quantitatively (volumetrically, see § 93) the strength of a dilute solution of nitrous acid.

#### NITRIC ACID, $\text{HNO}_3$ .

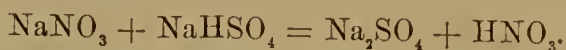
127. This is the best known acid of nitrogen. It is manufactured on a large scale, since its uses are many and varied; in the organic dyestuff industry, for example, large quantities are employed. The commercial process of manufacture depends on the decomposition of Chili saltpetre,  $\text{NaNO}_3$ , by strong sulphuric acid:



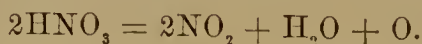
It is carried out in the following way:

In the cast-iron retort (*C*, Fig. 44), saltpetre and sulphuric acid (chamber-acid) are mixed in proportions corresponding to the above equation, a slight excess of sulphuric acid, however, being added, because this makes the residue easier to remove from the retort. The retort is connected with a row of earthenware bottles (*EE'*) containing a little water. These receive the distilled acid. The last bottle connects with a coke tower through which water is trickling down to dissolve the uncondensed acid vapor. By this process a liquid of a specific gravity of 1.35 and containing 60% acid is obtained. If the saltpetre is previously dried and concentrated sulphuric acid is used, a nitric acid of sp. g. 1.52 and almost 100% pure can be obtained.

In some cases two molecules of saltpetre are used to one of sulphuric acid. If heat is moderately applied, the process is the same as above, but on heating to a higher temperature the acid sodium sulphate that is formed acts on the second molecule of nitrate, also forming nitric acid:



A large part of the nitric acid, however, dissociates at the same time as follows:



The  $\text{NO}_2$ -fumes dissolve in the distillate. The liquid thus

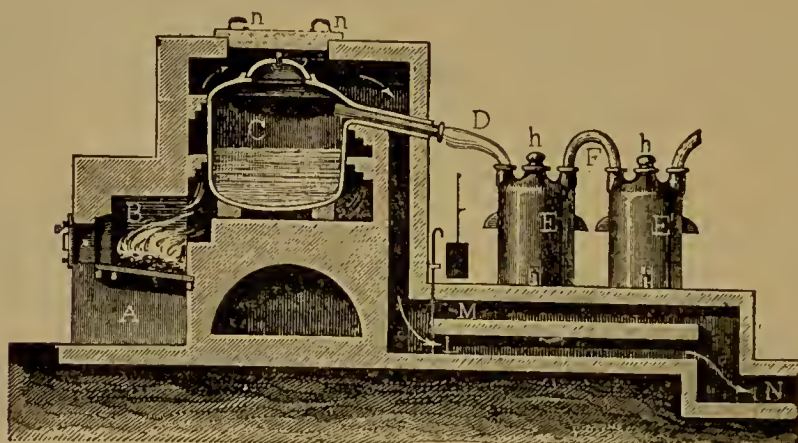


FIG. 44.—MANUFACTURE OF NITRIC ACID.

obtained is red and its specific gravity is 1.52–1.54; it fumes strongly in the air and is known as “*red fuming nitric acid.*”

For some years the distillation of saltpetre with sulphuric acid has been carried on in a vacuum. The yield of acid in such a case approaches closely to the theoretical and the product obtained is entirely free from nitrous fumes. The latter result is also accomplished by the use of a tube condenser (HART) instead of bottles.

Nitric acid is formed in small amounts in certain processes of burning in the air, e.g. when hydrogen is exploded with air, when sparks pass through moist air for some time, in the combustion of ammonia, etc. CROOKES has shown that nitrogen is combustible; when a spark from a strong induction coil is sent between two terminals, the air takes fire, or more correctly the nitrogen, and

burns with a vigorous flame, producing nitrous and nitric acids. The reason why the flame does not spread farther over the earth and the earth is not flooded with nitric acid lies in the fact that the kindling-point is far above the temperature of the flame. Nitric acid also results from the action of certain sorts of bacteria, which serve as conveyers of oxygen, when nitrogenous organic substances are left exposed to the air in contact with basic substances, such as lime; this was formerly the method of preparing saltpetre on a large scale (§ 229).

*Physical Properties.*—Absolute nitric acid, i.e. the compound  $\text{HNO}_3$  in the pure state, is prepared by distilling the nearly pure acid of commerce (sp. g. 1.5) with concentrated sulphuric acid *in vacuo*. The liquid distillate has a specific gravity of 1.559 at  $0^\circ$  and becomes solid at  $-40^\circ$ ; it boils under ordinary pressure at  $86^\circ$ , but with partial decomposition.

*Chemical Properties.*—Nitric acid, especially when pure, is a rather unstable compound; at ordinary temperatures it is decomposed by sunlight to a slight extent, turning yellow on account of the small amount of nitrogen dioxide formed. At an elevated temperature the acid also breaks up, decomposition into  $\text{NO}_2$ ,  $\text{H}_2\text{O}$  and O being complete at  $260^\circ$ .

When strong nitric acid is subjected to repeated distillation under atmospheric pressure, its boiling-point gradually rises, while the acid becomes proportionately weaker, until finally a 68% acid is obtained, which boils constant at  $120.5^\circ$ . The same mixture is obtained when one starts with dilute acid and distills it. We have here phenomena analogous to those attending the distillation of hydrochloric acid (§ 29).

Nitric acid is very extensively split up into ions in its aqueous solution; it is one of the strongest acids known.

When it comes in contact with metals, the salts of nitric acid (nitrates) are formed, but without any evolution of hydrogen, since part of the acid present is reduced by the nascent hydrogen. The nitrates are all easily soluble in water. The action of nitric acid on the metals is not the same in all cases. It does not attack gold or platinum. Silver, mercury and copper are only imperceptibly dissolved at ordinary temperatures, but on warming they dissolve with the evolution of nitric oxide. This and the other NO-compounds are powerful catalyzers in the dissolving of the above-named metals, for nitric acid which is perfectly free from

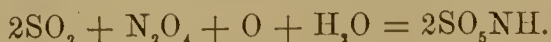
them does not dissolve these metals, while the reaction immediately begins as soon as a little of these substances is added. It may be supposed that on warming nitric acid a trace of NO-compounds is formed, which together with the elevation of the temperature accelerates the reaction. Iron, zinc and magnesium reduce nitric acid to nitrous oxide and even to ammonia. Under the action of iron-filings and dilute sulphuric acid the reduction of nitric acid to ammonia in dilute solution is quantitative. There are also various denitrifying bacteria known, the *Bac. pyocyaneus* being the best studied of them.

Nitric acid frequently acts as a powerful oxidizing agent, especially at an elevated temperature. If sulphur is boiled with it, the sulphur is converted to sulphuric acid, similarly phosphorus to phosphoric acid. A glowing piece of charcoal, dropped upon the concentrated acid, continues to burn with a bright glow. In all these cases the highest oxidation-stages are formed. Nitric acid is used particularly in the organic branches of chemical industry.

The *composition* of nitric acid can be deduced from that of its anhydride. A weighed amount of the latter is introduced into water; nitric acid is formed, which is neutralized with baryta water. By evaporation it is possible to determine how many parts by weight of barium oxide, BaO, combine with anhydride. It is found that 153.2 parts (= 1BaO) combine with 108.08 parts (= 1N<sub>2</sub>O<sub>5</sub>); the formula of barium nitrate thus becomes Ba(NO<sub>3</sub>)<sub>2</sub>, hence that of nitric acid itself must be HNO<sub>3</sub>.

### Derivatives of the Nitrogen Acids.

128. In discussing the manufacture of sulphuric acid (§ 86) we already referred to the **chamber crystals**, HSO<sub>5</sub>N. They are formed in the lead-chambers in case not enough steam is supplied. The following equation expresses the action that takes place:

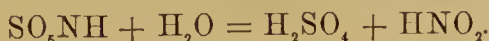


The ordinary method of preparing this substance is by conducting carefully dried sulphurous oxide into cooled fuming nitric acid:



The crystalline mass obtained is spread out on porous earthenware to allow the adhering liquid to be absorbed.

The chamber crystals have the appearance of a coarse crystalline, colorless mass; they melt at 73°. They are at once decomposed by water into sulphuric and nitrous acids:

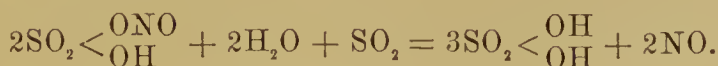


For this reason the compound is considered as the *mixed anhydride of sulphuric and nitrous acids*. According to § 90 the structure  $\text{SO}_2 < \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$  can be ascribed to sulphuric acid; to nitrous acid the structure HO-NO, since a hydroxyl is assumed (§ 129) to exist in it. For the chamber crystals we therefore have



Since the atomic group NO is known as *nitrosyl*, the rational name for the compound is *nitrosyl sulphuric acid*.

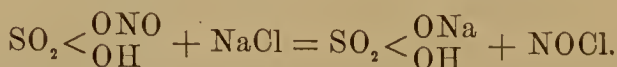
Concentrated sulphuric acid dissolves nitrosyl sulphuric acid without change. This solution is very stable; it can be distilled without decomposition. It is formed in the Gay Lussac tower of the sulphuric-acid factory and is called "nitrated acid" or "nitrous vitriol". On dilution with water this solution is not altered until its specific gravity reaches 1.55–1.50 (51°–48° B.); then the nitric oxides begin to escape, especially when warmed. Water and sulphurous oxide act on the nitrated acid, producing the following reaction:



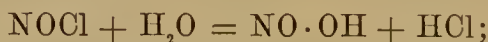
This action takes place in the Glover tower.

It is of great importance industrially to be able to determine the amount of nitrogen that the nitrated acid contains. This can be done as follows: The acid is agitated with mercury, whereby all nitrogen compounds in solution are given off in the form of nitric oxide, and the gas evolved is measured. Another method consists in decomposing the nitrated acid with a large excess of water and titrating with permanganate the nitrous acid formed (§ 126).

129. Nitrosyl chloride, NOCl, is a reddish-yellow gas at ordinary temperatures; by cooling to  $-20^{\circ}$  it can be condensed to a red liquid, that boils at  $+2^{\circ}$ . This compound is formed by the direct combination of NO and Cl. The best method of preparation, however, is that of carefully warming chamber crystals with thoroughly dried sodium chloride:

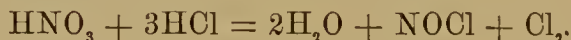


Nitrosyl chloride is broken up by water into nitrous and hydrochloric acids:



hence it may be regarded as the chloride of nitrous acid (§ 130).

On mixing hydrochloric acid with nitric acid a liquid is produced which, in addition to these two acids, contains chlorine and nitrosyl chloride:

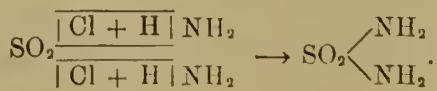


This liquid (by virtue of the free chlorine it contains) dissolves the precious metals, including gold, the "king" of the metals; it therefore bears the name *aqua regia*. It was known even to the alchemists, particularly GEBER, who prepared it by dissolving sal ammoniac,  $\text{NH}_4\text{Cl}$ , in nitric acid.

#### OTHER NITROGEN COMPOUNDS.

130. In organic chemistry acid derivatives are known, which are formed through the substitution of the hydroxyl group by a halogen atom or the amido group  $\text{NH}_2$ . The former class are called acid chlorides, the latter amides. Of the inorganic acid chlorides we have already become acquainted with those of sulphuric acid (§ 90). Nitrosyl chloride is also an acid chloride. A few inorganic acid amides will now be discussed briefly.

By the action of ammonia gas on a solution of sulphuryl chloride in chloroform there is formed among other things sulphamide,  $\text{SO}_2(\text{NH}_2)_2$ .



This compound forms large colorless crystals that are very soluble in

water and melt at 81°. It is transformed by alkalis into an amido-sulphonate,  $\text{SO}_2 < \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$ . This acid is very stable, is slightly soluble in water, and crystallizes in colorless rhombic prisms.

Potassium sulphite and potassium nitrite react to form a crystalline precipitate; this compound, to which is given the structural formula  $\text{N}(\text{SO}_3\text{K})_3 + 2\text{H}_2\text{O}$ , is regarded as ammonia in which three hydrogen atoms are replaced by sulpho groups ( $\text{SO}_3\text{K}$ ):



It is known as potassium nitrilosulphonate. On boiling it for a short time with water, or better, by letting it stand for a day moistened with dilute sulphuric acid, it forms potassium imidosulphonate:



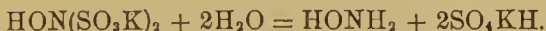
If the boiling is continued for a long period, amidosulphonic acid is produced:



Similar derivatives of hydroxylamine are also known. The potassium salt of hydroxylamine-disulphonic acid,  $\text{HO}\cdot\text{N}(\text{SO}_3\text{K})_2 + 2\text{H}_2\text{O}$ , is formed when solutions of acid potassium sulphite and potassium nitrite are mixed:



By boiling this compound with water hydroxylamine is set free:



The amide of nitric acid, nitramide,  $\text{NH}_2\text{-NO}_2$ , has so far been obtained only from an organic compound, nitrourethane,  $\text{NO}_2\text{NH}\cdot\text{CO}_2\text{C}_2\text{H}_5$ . This amide appears in colorless crystals that melt at 72° with decomposition. The aqueous solution reacts strongly acid. It is a very unstable substance, decomposing on being mixed with copper oxide, powdered glass or the like. It is immediately broken up by alkalis and even by sodium acetate at ordinary temperatures, nitrous oxide and water being formed in the latter case.

## PHOSPHORUS.

131. Phosphorus does not occur free in nature, inasmuch as it combines very easily with oxygen. Nevertheless salts of phosphoric acid are widely distributed and occur in large quantities. Tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , *phosphorite*, is found in large deposits; other phosphates which are frequently met with are:

*apatite*,  $3\text{Ca}_3(\text{PO}_4)_2 + \text{CaCl}_2$  (or  $\text{CaF}_2$ ); *wavellite*,  $4\text{AlPO}_4 + 2\text{Al}(\text{OH})_3 + 9\text{H}_2\text{O}$ ; and *vivianite*,  $\text{Fe}_3(\text{PO}_4)_2 + 8\text{H}_2\text{O}$ . Phosphates are also found to a small extent in granite and volcanic rocks; when these decay they enter the soil. About 0.1% phosphates (calculated as  $\text{P}_2\text{O}_5$ ) is present in soil of average fertility. Bones contain a considerable proportion of tricalcium phosphate.

Phosphorus has been known for a long time. In 1674 the

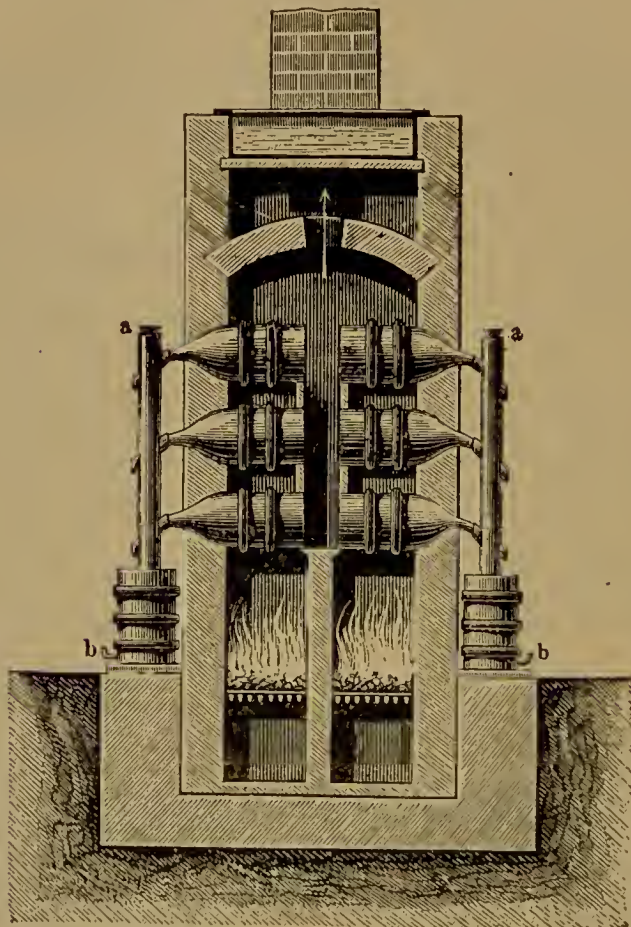


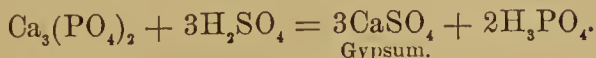
FIG. 45.—MANUFACTURE OF PHOSPHORUS.

alchemist BRAND discovered it at Hamburg by evaporating urine and heating the residue with sand in an earthen retort. SCHEELÉ first prepared phosphorus from bones by a process which in the main is still employed.

For the *manufacture of phosphorus* bones or phosphorite are used. By treatment with sulphuric acid gypsum and phosphoric



acid are formed; the former is precipitated so that the solution of phosphorus can be easily poured off:



This solution is evaporated to a sirupy consistency, mixed with about one-fourth its weight of coke or charcoal and carefully dried in iron vessels, by which process the orthophosphoric acid,  $\text{H}_3\text{PO}_4$ , is converted into metaphosphoric acid,  $\text{HPO}_3$ . The dry mixture is then heated in clay retorts, such as are pictured in Fig. 45, the following reaction taking place:



The phosphorus vapor, hydrogen and carbon monoxide escape through the earthenware pipe *a*, which opens under water into the vessels *bb*, in which the phosphorus vapor is condensed.

Before the bones are used they are subjected to various preliminary operations. In some cases the fats are first extracted (with benzine) and then treated with high-pressure steam, whereby the organic portion (the cartilaginous matter) is converted into glue. The residue consists almost wholly of calcium phosphate and carbonate, and is worked up into phosphorus as above explained.

In other instances the bones are subjected to a dry distillation, from which "DIPPEL'S *animal oil*" is obtained, containing a number of important organic bases. That which remains in the retorts is *bone-black* (animal charcoal), which is used in large quantities in sugar-factories to decolorize the sugar solutions. After it is no longer of use for this purpose, the animal charcoal is burned in the air, the carbon being consumed and white boneash remaining. This boneash is then sent to the phosphorus-factory.

By using the heat of the electric arc phosphorus is now being manufactured from calcium phosphate, sand and charcoal.

The phosphorus thus obtained is black because of adhering particles of charcoal and contains still other impurities. It can be purified by fusing it under water and pressing it through chamois; this process is usually preceded by a washing with a dilute solution of sulphuric acid and potassium bichromate, whereby the impurities are oxidized out. Finally the phosphorus is cast into sticks and in this form enters the market.

132. *Physical Properties.*—At ordinary temperatures phosphorus is a crystalline solid of a light yellow color and having a specific gravity of 1.83 at 10°. When cold it is brittle on account

of its crystalline texture; above  $15^{\circ}$  it becomes soft and waxy and melts at  $44.4^{\circ}$  to a yellow, strongly refractive liquid. Its boiling-point is  $290^{\circ}$ ; it then turns to a colorless vapor. In the sunlight it becomes yellow and coated with an opaque pink layer. Phosphorus is insoluble in water, slightly soluble in alcohol and ether, but easily soluble in carbon bisulphide, from which it crystallizes in regular crystals.

The *vapor density* of phosphorus at temperatures between  $515^{\circ}$  and  $1040^{\circ}$  is 4.58–4.50 (air = 1). Its molecular weight is therefore 123.84. Inasmuch as the smallest amount of phosphorus that is found in one gram-molecule of any of the numerous phosphorus compounds investigated is 31 g., this number therefore represents the atomic weight of the element; hence the molecule must consist of  $\frac{123.84}{31} = 4$  atoms. Between  $1500^{\circ}$  and  $1700^{\circ}$  the vapor density decreases considerably, but does not quite reach the value corresponding to  $P_2$  molecules. By the cryoscopic method (§ 43) it has been found that the molecule of phosphorus also consists of four atoms at ordinary temperatures.

**133. Allotropic Forms.**—**Ordinary**, or **yellow phosphorus** can be transformed by heating to  $250^{\circ}$ – $300^{\circ}$  (in absence of air, necessarily) into a reddish-brown powder, **red phosphorus**. Iodine is an accelerator of this process, so that a very small quantity makes it possible for this transition to take place even below  $200^{\circ}$ . Red phosphorus is manufactured on a large scale by heating the yellow form in sealed iron cylinders for a few minutes at  $250^{\circ}$ – $300^{\circ}$ . After cooling the product is treated with carbon bisulphide and with caustic soda in order to extract the unchanged yellow phosphorus.

Red phosphorus is considerably different in its properties from the yellow form. It is not poisonous, while the latter is very much so. Red phosphorus is unaffected by the air and has not been melted. Its specific gravity is 2.106; it is insoluble in carbon bisulphide. RETGERS has shown that it is in part crystalline. Moreover it is odorless, while yellow phosphorus gives off a peculiar odor because of the formation of ozone (§ 36). When heated in the air, it does not ignite till  $260^{\circ}$  is reached. On the whole it is chemically much less active than yellow phosphorus.

The yellow modification can be kept for an unlimited period at ordinary temperatures; nevertheless it must be regarded as an

unstable form, just like "detonating gas," for at an elevated temperature (the higher, the faster), both pass over into a more stable form with the evolution of heat. The relative stability of the yellow form is only a consequence of the extraordinarily small velocity with which the transformation into the red one takes place at ordinary temperatures. Yellow phosphorus can be regained from the red by distilling the latter and cooling the vapor rapidly. It is a general rule that where a substance exists in different forms, the least stable appears first. Now, if the temperature is low, the velocity of transformation of the yellow form is so small that it seems perfectly stable.

**Metallic phosphorus** is obtained by heating phosphorus with lead in evacuated air-tight tubes for ten hours at the temperature of faint red heat. The lead is then found permeated with very dark-hued small crystals, which can be separated out by dissolving the lead in dilute nitric acid. This modification has a specific gravity of 2.34. It is probable that metallic and red phosphorus are identical, only the former is better crystallized.

**134. Chemical Properties.**—Phosphorus has a great affinity for many elements; it combines directly with all elements except nitrogen and carbon, the combination occurring with great vigor in many cases, e.g. when phosphorus is brought in contact with sulphur or bromine. Certain compounds of the metals (phosphides) are known, which are called *phosphorus bronzes* (§ 199). Especially characteristic of phosphorus is its very strong affinity for oxygen; yellow phosphorus takes fire in the air at  $40^{\circ}$ , so that contact with a hot glass rod is sufficient to ignite it. The burning is accompanied by a vigorous evolution of light and heat, phosphorus pentoxide,  $P_2O_5$ , being formed. On account of this strong affinity for oxygen phosphorus is a powerful reducing agent. Sulphuric acid, when warmed with it, is reduced to sulphur dioxide; concentrated nitric acid oxidizes it with explosive violence; dilute acid evolves nitrous fumes, oxidizing the phosphorus to phosphoric acid. Many metals are precipitated by phosphorus from their salts, phosphides being formed to some extent. Silver nitrate, for instance, gives silver and  $Ag_3P$  with phosphorus; on warming phosphorus with a solution of copper sulphate copper phosphide,  $Cu_3P_2$ , is deposited.

**135.** The slow oxidation of phosphorus by oxygen at ordinary temperatures is accompanied by the emission of a bluish light. This *luminosity of phosphorus* is very plain in the dark.

This phenomenon is due to various circumstances, some of which are very mysterious. The oxidation, and hence the luminosity, is prevented by the presence of traces of certain substances, such as hydrocarbons, ammonia, etc. Further, the luminosity depends on the temperature; below  $10^\circ$  it is extremely weak. The gas-pressure has a peculiar influence; at ordinary temperatures phosphorus does not emit light in pure oxygen of atmospheric pressure, but if the pressure is reduced, a point is reached at which luminosity commences; this is at 666 mm. for  $15^\circ$ , and at 760 mm. for  $19.2^\circ$ . The oxidation is therefore more vigorous in dilute oxygen (i.e. oxygen mixed with another gas, as nitrogen) than in concentrated. VAN MARUM observed as early as 1798 that a piece of phosphorus laid on wadding (which serves as a poor conductor of heat) in a closed vessel shines the more brightly as the oxygen is pumped out, and may even take fire in very dilute gas.

The fact that oxidations are more energetic under reduced oxygen-pressure has been observed in many other cases. Some of these (for instance, the oxidation of acetaldehyde to acetic acid) are simple enough to be studied quantitatively, and it has been found that the reaction-velocity is proportional to the square root of the pressure of the oxygen. This can be explained by the supposition that the oxygen molecules are split up to a very small extent into their atoms and that these alone cause the oxidation. The equilibrium that must then exist between the atoms and molecules of the oxygen and is represented by



is mathematically expressed by the equation (§ 51):

$$C_{(\text{O}_2)} = k \cdot C_{(\text{O})}^2,$$

where  $C_{(\text{O}_2)}$  is the concentration of the molecules,  $C_{(\text{O})}$  that of the atoms, and  $k$  a constant. From this equation we have

$$C_{(\text{O})} = k \cdot \sqrt{C_{(\text{O}_2)}}.$$

The concentration of the oxygen molecules can be regarded as proportional to the total pressure, the quantity of O-atoms being anyhow very small; hence the second equation also shows that the concentration of the oxygen atoms is proportional to the root of the pressure, as was found by experiments.

Still another curious phenomenon is observed during the slow oxidation of many substances, organic as well as inorganic: when oxidation takes place in the presence of another easily oxidizable compound (called the *acceptor*) the latter takes just as much oxygen as is used for the oxidation. The following example may illustrate this. Sodium

sulphite is easily oxidized by free oxygen (§ 84) to sodium sulphate. On the other hand sodium arsenite is not oxidized by free oxygen when its solution contains an excess of  $\text{KHCO}_3$ . But when solutions of sodium sulphite and sodium arsenite are mixed and then shaken with air, just as much oxygen is used for the oxidation of the acceptor (the arsenite) as for that of the sulphite. In other words, the sulphite, on being oxidized, has *activated* the same quantity of oxygen as it has taken itself. To explain this, VAN'T HOFF supposes that the parts into which the oxygen molecule is split up, are not atoms but ions; as they have opposite electrical charges, it is to be conceived that the oxidizable compound takes only one kind of ions, the acceptor the other.

*Detection of Phosphorus.*—Poisonings by yellow phosphorus occur now and then. In order to detect it in such cases, use is made of its luminosity. For this purpose the contents of the stomach, which are to be tested for phosphorus, are diluted with water in a distilling-flask, connected with a condenser by a tube doubly bent at right angles. On heating the flask water distills over with a little phosphorus vapor; if the whole apparatus is placed in a dark room, a luminous ring is noticed during this distillation at the place where the steam is condensed, i.e. where the phosphorus vapor comes in contact with air in the condenser. The distillate contains phosphoric acid (MITSCHERLICH'S test).

*Use.*—Phosphorus is used chiefly for the manufacture of matches. Matches of the old sort are prepared by dipping the ends of the sticks first in molten sulphur and then in a paste consisting of gum, an oxidizing-agent (e.g. manganese dioxide) and yellow phosphorus. By rubbing them on a rough surface enough heat is generated to set them afire. These matches are not only very poisonous on account of the yellow phosphorus they contain but also very inflammable. Moreover, their manufacture is very injurious to the health of the workmen. For this reason in some countries (e.g. in the Netherlands) their manufacture is prohibited by law. They are being gradually displaced, especially in European countries, by the Swedish safety-matches, which lack this defect. In them the head consists chiefly of a mixture of potassium chlorate and antimony sulphide. They are lighted by striking them on a surface coated with some red phosphorus. To be sure, their use has the disadvantage of requiring a special surface to ignite them on, but this on the other hand excludes the possibility of ignition by accidental friction.

### Compounds of Phosphorus and Hydrogen.

There are three compounds of phosphorus and hydrogen known: (1) *gaseous* hydrogen phosphide,  $\text{PH}_3$  (also called phosphine); (2) *liquid* hydrogen phosphide,  $\text{P}_2\text{H}_4$ ; and (3) *solid* hydrogen phosphide,  $(\text{P}_2\text{H})_x$ .

#### HYDROGEN PHOSPHIDE. PHOSPHINE. $\text{PH}_3$ .

136. This compound can be prepared from the elements by bringing phosphorus together with zinc and dilute sulphuric acid, i.e. with nascent hydrogen; when thus prepared, it is mixed with a large quantity of hydrogen.

It is obtained perfectly *pure* by decomposing phosphonium

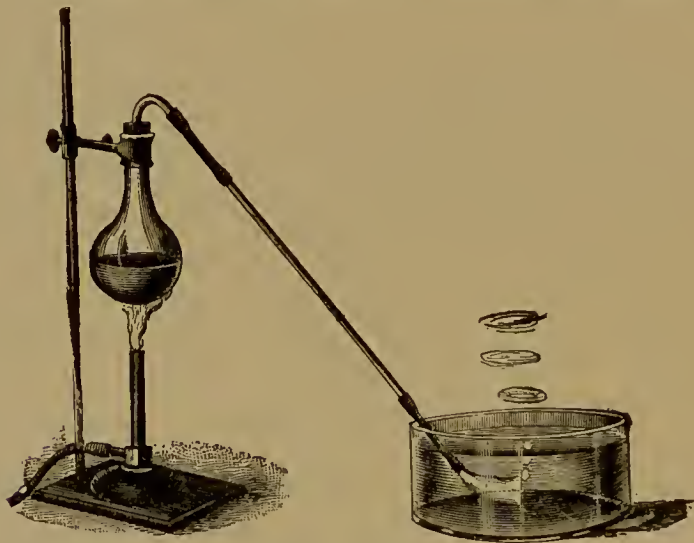
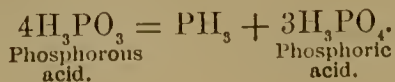


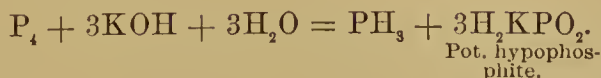
FIG. 46.—PREPARATION OF HYDROGEN PHOSPHIDE.

iodide,  $\text{PH}_4\text{I}$  (see below); this substance, when treated with water or caustic potash, breaks up into phosphine and hydrogen iodide; the former passes off, while the latter stays in the liquid.

The generation of hydrogen phosphide by heating phosphorous and hypophosphorous acids is another example of its formation by the direct decomposition of phosphorus compounds:



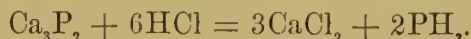
The ordinary method of preparation is by the action of phosphorus on caustic potash:



The reaction is really more complicated than this equation indicates, for in addition hydrogen,  $P_2H_4$ , and other substances are formed. (See also § 144.)

By reason of the presence of gaseous  $P_2H_4$ , which is self-inflammable, each bubble of gas ignites as it breaks into the air, forming usually a smoky ring of phosphorus pentoxide (Fig. 46). On account of this inflammability the vessel in which the gas is generated from phosphorus and caustic potash must be as full of liquid as possible. Moreover, the delivery-tube (preferably with a wide mouth) must open in *warm* water, in order that it may not become clogged with particles of phosphorus carried over. By passing the gas through hydrochloric acid or alcohol, the hydrogen phosphide is freed from  $P_2H_4$  and is then no longer spontaneously combustible.

No method of producing hydrogen phosphide by the action of hydrogen on phosphorus compounds is known; however, we have one by the interaction of hydrogen compounds and phosphorus compounds. Calcium phosphide, when decomposed by water or dilute hydrochloric acid, forms hydrogen phosphide:

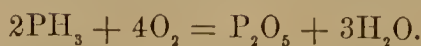


The phosphides of zinc, iron, tin and magnesium are decomposed by dilute acids with the formation of hydrogen phosphide.

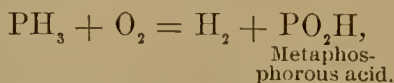
*Physical Properties.*—Hydrogen phosphide, or phosphuretted hydrogen,  $PH_3$ , is a gas at ordinary temperatures; it becomes liquid at  $-85^\circ$  and solid at  $-133.5^\circ$ . It has a peculiar disagreeable odor, that reminds one of spoiled fish. It is slightly soluble in water, more so in alcohol. Sp. g. = 17 (O = 16).

**137. Chemical Properties.**—Hydrogen phosphide is very poisonous; it burns very easily, yielding phosphoric acid. In the presence of oxygen of ordinary pressure it remains unchanged; if, however, the pressure is diminished, an explosion results. This conduct reminds one of phosphorus, which is luminous (because of oxidation) only below a certain limit of pressure (§ 135).

The combustion of hydrogen phosphide may be expressed by the equation:



Accordingly the reaction would be hexamolecular (§ 50). VAN DER STADT demonstrated by a method, similar to that referred to in § 51, that the first stage of the reaction is bimolecular and corresponds very closely to the following equation:



if the gases slowly diffuse into each other in a diluted condition.

In general, experience has taught that the mechanism of a reaction is decidedly simple and that chemical processes are almost always mono- or bimolecular. Accordingly, when the quantitative course of a reaction is represented by an equation indicating the participation of several molecules, it is probable that several intermediate reactions are involved.

Hydrogen phosphide can unite with halogen-hydrogen acids directly to form compounds of the type  $\text{PH}_4\text{X}$  ( $\text{X} = \text{halogen}$ ), in analogy with ammonia. The best known of these compounds is  $\text{PH}_4\text{I}$ , **phosphonium iodide**, a colorless, well-crystallized compound, which is formed when dry hydrogen phosphide and hydrogen iodide are mixed.

An easier method of preparation is to treat a solution of yellow phosphorus in carbon bisulphide with iodine, distill off the carbon bisulphide and then add water slowly, warming gently; phosphonium iodide sublimes out. The equation is



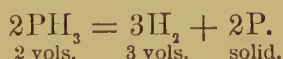
Phosphonium iodide is very unstable, as was mentioned in § 136; this is even more the case with phosphonium bromide, which is also a solid but is completely dissociated into the two hydrogen compounds,  $\text{PH}_3$  and  $\text{HI}$ , as low as  $30^\circ$ . Phosphonium chloride is dissociated even at ordinary temperatures and pressures and can only exist below  $14^\circ$  or under more than 20 atm. pressure. Considering these properties, it is not surprising that phosphonium,  $\text{PH}_4^+$ ,—like ammonium—should be impossible to isolate. No other acids except those mentioned unite with



hydrogen phosphide. The general behavior of the latter thus shows that it is very much less basic than ammonia.

Hydrogen phosphide possesses reducing properties. From solutions of silver nitrate or copper sulphate it precipitates a mixture of metal and phosphide; this property can be made use of to separate the gas from other gases. When mixed with chlorine it explodes vigorously; forming hydrochloric acid and phosphorus trichloride.

The *composition* of hydrogen phosphide was determined by passing a known volume over copper turnings in a heated tube. The copper combines with the phosphorus, so that the increase in weight of the tube shows the proportion of phosphorus. The escaping hydrogen is collected and measured. In the experiment it was found that 34 parts (by weight) of hydrogen phosphide contain 31 parts of phosphorus and 3 parts of hydrogen, so that, by comparing this with the atomic weights, the empirical formula is found to be  $\text{PH}_3$ . This also expresses the molecule, for the specific gravity of the gas is 17 ( $\text{H} = 1$ ), its molecular weight therefore 34. This agrees with the results of the decomposition of hydrogen phosphide by induction sparks or by the electric arc; 1 vol.  $\text{PH}_3$  yields  $1\frac{1}{2}$  vols. hydrogen and also amorphous phosphorus, which is deposited on the sides of the tube and on the platinum wires (or carbons).



#### Liquid Hydrogen Phosphide, $\text{P}_2\text{H}_4$ .

138. In certain cases this compound is formed as a by-product in the preparation of phosphine. Especially is it formed in the decomposition of calcium phosphide with water. It also results from the oxidation of phosphine by various substances, for instance, nitrogen dioxide, by which ordinary hydrogen phosphide can be made spontaneously inflammable. The mixture of  $\text{PH}_3$  and  $\text{P}_2\text{H}_4$  can be separated by passing it through a well-cooled tube; the latter condenses to a colorless liquid, which boils at  $57^\circ$ – $58^\circ$  (under 735 mm.) and has a specific gravity of 1.01. It is easily decomposable and cannot be preserved, because it rapidly changes to the gaseous and the solid hydrogen phosphides. The same decomposition is also effected by hydrochloric acid. It must be condensed in the dark, as sunlight aids decomposition. The empirical composition is indicated by the formula  $\text{PH}_2$ ; but since phosphorus is trivalent, we take  $\text{P}_2\text{H}_4$ , i.e.

$H_2P-PH_2$ , as the formula of the molecule. Liquid hydrogen phosphide thus becomes analogous to hydrazine.

#### Solid Hydrogen Phosphide ( $P_2H$ )<sub>x</sub>.

139. This substance is formed by the decomposition of the preceding one, especially easily when phosphine charged with  $P_2H_4$  vapor is led into concentrated hydrochloric acid. It then separates as a yellow powder of the empirical formula  $P_2H$ , whose molecular weight it has as yet been impossible to ascertain. On being heated (in a  $CO_2$ -atmosphere) it breaks up into phosphorus and hydrogen; when heated in the air it catches fire at  $160^\circ$ . It is insoluble in water.

#### Halogen Compounds of Phosphorus.

Phosphorus unites with all four of the halogens to form compounds of the types  $PX_3$  and  $PX_5$ ; the most important are the chlorides.

#### PHOSPHORUS TRICHLORIDE, $PCl_3$ .

140. This compound can only be obtained by direct combination of the elements. In preparing it a rapid current of dry chlorine is led over phosphorus in a retort. The phosphorus burns with a pale yellow flame and a mixture of trichloride and pentachloride distills over into the receiver, which is kept cold. A little phosphorus is added to the distillate in order to convert the pentachloride to trichloride, and the liquid is redistilled. An easier method is to introduce phosphorus into a flask with some phosphorus trichloride and lead chloride into the mixture.

*Physical Properties.*—Phosphorus trichloride is a colorless liquid of a very pungent odor; it boils at  $76^\circ$  and remains liquid as low as  $-115^\circ$ . Sp. g. 1.61294 at  $0^\circ$ .

*Chemical Properties.*—Water decomposes it very rapidly with the formation of hydrochloric and phosphorous acids:



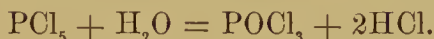
it is because of this decomposition that it fumes in moist air. Continued treatment with chlorine converts it into the pentachloride.

#### PHOSPHORUS PENTACHLORIDE, $PCl_5$ .

141. This substance is prepared by passing chlorine over phosphorus trichloride. Fine light yellow crystals at once appear and the entire mass finally becomes solid, indicating that all is con-

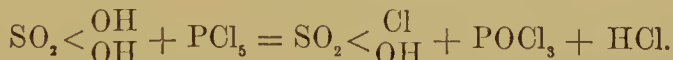
verted into pentachloride. This compound fumes strongly in moist air, being immediately decomposed by water with the formation of hydrochloric and phosphoric acids. When heated it sublimes without melting. In the transition to the gaseous state it breaks up at a rather low temperature into the trichloride and chlorine; this dissociation is complete at  $300^{\circ}$ , for at that point the vapor density is just half of that calculated for the pentachloride. The vapor, which at moderately low temperatures is almost colorless, takes on the yellow color of chlorine for the above reason, as the temperature rises. The dissociation products, phosphorus trichloride and chlorine, can be separated by diffusion. Phosphorus pentachloride evaporates in an atmosphere of the trichloride with almost no dissociation (*cf.* § 51).

By the addition of a little water it is converted into phosphorus oxychloride:



With more water phosphoric and hydrochloric acids are produced.

Phosphorus pentachloride is used in organic chemistry to replace hydroxyl groups with chlorine. In inorganic chemistry, it can also be employed for the same purpose; thus sulphuric acid reacts with it in the following manner (§ 90):



#### PHOSPHORUS OXYCHLORIDE, $\text{POCl}_3$ .

142. The best method of preparing this compound is by the oxidation of the trichloride with sodium chlorate:



In order to moderate the great vigor of this reaction sodium chlorate is placed under phosphorus oxychloride and the trichloride is then added slowly by means of a dropping-funnel. Besides the method just given, phosphorus oxychloride may be obtained by the hot digestion of the pentachloride with the pentoxide of phosphorus:



Phosphorus oxychloride is a colorless, mobile liquid, that boils at  $107.2^{\circ}$  and, when solid, melts at  $-1.5^{\circ}$ . Sp. g. = 1.7118 at  $0^{\circ}$ .

In the presence of water, with which it is not miscible, it slowly changes to phosphoric and hydrochloric acids:



#### THE COMPOUNDS OF PHOSPHORUS WITH THE OTHER HALOGENS.

143. These are very analogous to the chlorine derivatives. They are likewise prepared by direct synthesis from the elements. Inasmuch as the reaction is very vigorous, it has to be moderated by dissolving the phosphorus and the halogen separately in carbon bisulphide, slowly adding one to the other and then distilling off the solvent. The fluorides have special methods of preparation. These compounds are broken up by water like the corresponding chlorides, the fluorides, however, quite slowly.

The *composition of these compounds* can be ascertained in the following way: In the decomposition with water they yield phosphoric or phosphorous acid and a halogen acid, so that the quantities of phosphorus and halogen present can be found by determining the amounts of these acids. Moreover, the molecular weight can be obtained by measuring the vapor density, it being necessary to remember, however, that compounds of the type  $\text{PX}_5$  are usually dissociated in the gaseous state.

#### Oxygen Compounds of Phosphorus.

144. Four compounds of this class are known: *phosphorus monoxide*,  $\text{P}_4\text{O}$ ; *phosphorous anhydride*,  $\text{P}_4\text{O}_6$ ; *phosphorus tetroxide*,  $\text{P}_2\text{O}_4$ ; and *phosphorus pentoxide*, or *phosphoric anhydride*,  $\text{P}_2\text{O}_5$ . Only the last is of any great importance.

##### Phosphorus Monoxide, $\text{P}_4\text{O}$ .

This substance is formed when finely divided phosphorus is treated at ordinary temperatures with a solution of caustic alkali in aqueous alcohol. The phosphorus dissolves in this, coloring it deep red and generating hydrogen:  $\text{P}_4 + \text{H}_2\text{O} = \text{P}_4\text{O} + \text{H}_2$ . On acidifying this solution the phosphorus monoxide is precipitated. It is insoluble in all solvents except alcoholic potash, which dissolves it, assuming a dark-red color. When the red solution is warmed it becomes colorless; hydrogen and phosphine escape and hypophosphorous acid is formed:  $\text{P}_4\text{O} + \text{H}_2\text{O} = 2\text{P}_2\text{O} + \text{H}_2$ ;  $\text{P}_2\text{O} + 3\text{H}_2\text{O} = 2\text{H}_3\text{PO}_2$ .

##### Phosphorous Anhydride, $\text{P}_4\text{O}_6$ .

This compound is produced when phosphorus burns in a slow current of dry air in a tube. The principal product is phosphorus pentoxide, which can be collected by a wad of glass fibers. The phosphorous anhydride

goes off as a vapor and is condensed in a well-cooled tube. It is a white-waxy substance when thus formed but it can also be obtained in crystals; the latter melt at  $22.5^{\circ}$  and boil at  $173.1^{\circ}$  (in a nitrogen atmosphere). The vapor density has been found to be 109.7, while that calculated for  $P_4O_6$  is 110. On being heated to  $440^{\circ}$  it is decomposed to red phosphorus and phosphorus tetroxide. It turns yellow in the light, which explains the fact that phosphorus pentoxide sometimes takes on a yellow color. It dissolves slowly in cold water, forming phosphorous acid; with hot water it produces red phosphorus, self-inflammable hydrogen phosphide and phosphoric acid in a vigorous reaction. When heated to  $50^{\circ}$ - $60^{\circ}$  in the air it takes fire and burns to the pentoxide.

#### Phosphorus Tetroxide, $P_2O_4$ .

is obtained from the  $P_4O_6$  compound, as was stated above. It forms colorless glistening crystals, that break up in water into phosphorous and phosphoric acids. In this respect its conduct is analogous to that of nitrogen tetroxide, which yields nitrous and nitric acids with water.

#### PHOSPHORUS PENTOXIDE, $P_2O_5$ .

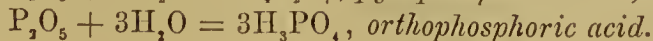
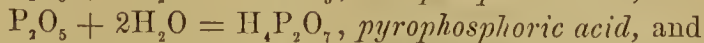
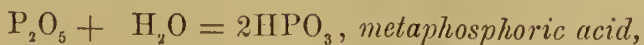
This compound is the product of the combustion of phosphorus in oxygen or an excess of dry air. It is a white, voluminous, snow-like mass, that takes up water rapidly to form phosphoric acid. It is the most powerful desiccating agent known. It exists in two modifications, both of which are formed simultaneously in the above process. The one is crystalline, subliming at  $250^{\circ}$ ; the other amorphous and not volatile below red heat; the vapor condenses crystalline. When heated above  $250^{\circ}$  the crystalline modification passes over into the amorphous.

Heating with charcoal reduces it to phosphorus.

The molecular weight of phosphorus pentoxide is not known; the formula  $P_2O_5$  is therefore empirical. It is very probable that the molecular weight is a multiple of it.

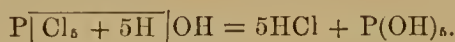
#### Acids of Phosphorus.

145. Only two of the above described oxides of phosphorus, viz.  $P_4O_6$  and  $P_2O_5$ , form corresponding acids; these oxides can unite with different amounts of water to form acids. From  $P_2O_5$  we have:

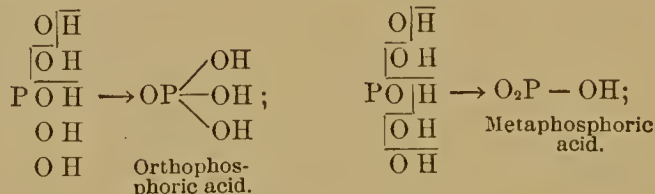


From the other oxide two acids can be derived: *metaphosphorous acid*,  $\text{HPO}_2$ , and *phosphorous acid*,  $\text{H}_3\text{PO}_3$ . Besides these there are two acids of phosphorus, whose anhydrides are unknown, viz. *hypophosphorous acid*,  $\text{H}_3\text{PO}_2$ , and *hypophosphoric acid*,  $\text{H}_4\text{P}_2\text{O}_6$ .

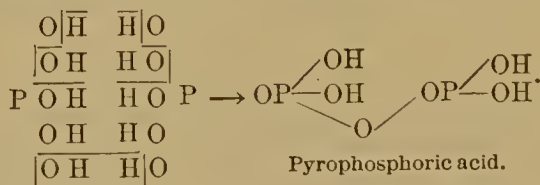
The relation between ortho-, meta- and pyrophosphoric acids can be shown in another way, which leads us to make some general observations. It was remarked in § 141 that phosphorus pentachloride is transformed by water into phosphoric and hydrochloric acids. The action of water on the pentachloride may be regarded as consisting first of a substitution of all five chlorine atoms by hydroxyl.



This compound, which would strictly be regarded as orthophosphoric acid, is unknown; a molecule of water is at once split off, forming the ordinary phosphoric acid,  $\text{H}_3\text{PO}_4$ , which we are accustomed to call orthophosphoric acid. In a similar way the metaphosphoric acid can be derived from the acid  $\text{P}(\text{OH})_5$  by the splitting off of two molecules of water:



while the pyrophosphoric acid can be regarded as  $2\text{P}(\text{OH})_5 - 3\text{H}_2\text{O}$ :



Orthophosphoric acid can also be derived from phosphorus oxychloride:



This way of looking at them makes plain not only the connection between the different acids, but also their structural formulæ. The same method can be applied to many other cases. As an example we may select the *per-iodic acids*. In § 62 only one was mentioned. There are salts, however, of various per-iodic acids, e.g.  $\text{MIO}_4$ ,  $\text{M}_3\text{IO}_5$ ,  $\text{M}_2\text{IO}_6$ , etc. These can be derived from a hypothetical acid  $\text{I}(\text{OH})_7$  in which iodine is

joined to as many hydroxyls as correspond to its maximum valence.  $M_5IO_6$  would be  $I(OH)_7 - 1H_2O$ ;  $M_3IO_5 = I(OH)_7 - 2H_2O$ ; and  $MIO_4 = I(OH)_7 - 3H_2O$ .

#### ORTHOPHOSPHORIC ACID, $H_3PO_4$ .

146. This acid can be obtained by direct synthesis from its elements; phosphorus burns to the pentoxide and the latter yields the acid on dissolving in water. Its formation by the action of nitric acid on phosphorus was mentioned in § 134. It can also be obtained by the oxidation of compounds containing phosphorus and hydrogen; phosphine and the lower acids of phosphorus are oxidized to phosphoric acid.

Ordinarily this acid is prepared by the oxidation of phosphorus with nitric acid or by liberating it from its salts, particularly the calcium salt,  $Ca_3(PO_4)_2$ . The latter is stirred into the theoretical amount of dilute sulphuric acid, forming calcium sulphate, which is only slightly soluble in water, and phosphoric acid, which goes into solution. On evaporating this solution the acid remains.

At ordinary temperatures orthophosphoric acid is a crystalline solid. It melts at  $38.6^\circ$ , is odorless and extremely soluble in water, forming a strongly acid solution.

It has the character of a strong acid; however, it is considerably less ionized than hydrochloric acid; a solution of 1 g.-mol. phosphoric acid in 10 l. water contains about one-fourth as many H ions as hydrochloric acid of the same molecular concentration. It is chiefly ionized into  $H^+$  and  $H_2PO_4^-$ . It generates hydrogen with metals, all three hydrogen atoms being replaceable by metallic atoms; it is therefore **tribasic**. Three classes of salts are possible and known to exist; these are the **primary**, **secondary** and **tertiary** salts. Of the alkali salts all three kinds are soluble; of the alkaline earth salts only the primary, the tertiary and secondary being insoluble. The other phosphates are insoluble in water but are dissolved by mineral acids.

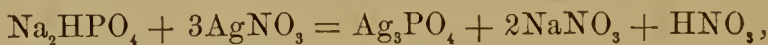
This latter property is due to the fact that phosphoric acid is a weaker acid than the strong mineral acids, hydrochloric, nitric and sulphuric. On treating an insoluble phosphate with one of these acids, e.g. hydrochloric, undissociated molecules of phosphoric acid are formed in the liquid; the more hydrochloric acid, the more the association, since the hydrochloric acid reduces the ionization of phosphoric acid.  $H_2PO_4^-$  and  $H^+$  ions thus disappear

and, in case enough hydrochloric acid is added, the concentration of the  $\text{H}_2\text{PO}_4'$  ions remaining will not be great enough together with that of the metal ions present to reach the value of the solubility product; hence all the phosphate must dissolve (§ 73).

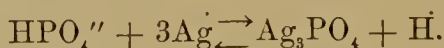
„ For the same reason, *as a general rule, salts that are insoluble in water will only dissolve in such acids as are stronger than the acid of the salt.* The only exception to this is when the value of the solubility product of the insoluble salt is very small, examples of which we have seen in certain sulphides (§ 73).

When heated to  $213^\circ$  orthophosphoric acid gives off water, forming mainly the pyro-acid but also a little meta-acid throughout the reaction. The pyro-acid on the other hand is converted by farther heating into the meta-acid.

With silver nitrate orthophosphates give a yellow precipitate of silver phosphate,  $\text{Ag}_3\text{PO}_4$ , soluble in nitric acid and ammonia. In the case of a primary or secondary phosphate, the precipitation is not complete, since nitric acid is liberated in the reaction:



or, expressed in ions:



If, however, an excess of sodium acetate is added, the precipitation is practically complete.

The reason for this is obvious. By the addition of acetate the acetic anions  $\text{C}_2\text{H}_3\text{O}_2'$  are forced to combine with the  $\text{H}$  ions, for acetic acid is only very slightly ionized and its ionization is moreover considerably lessened by the excess of sodium acetate. The result is that in the equilibrium  $\text{HPO}_4'' + 3\text{Ag} \rightleftharpoons \text{Ag}_3\text{PO}_4 + \text{H}$  the  $\text{H}$  ions are removed. The inverse reaction  $\leftarrow$  is then no longer possible, and the reaction  $\rightarrow$  must therefore become complete, or in other words all the phosphoric acid is precipitated as silver phosphate.

Phosphoric acid is precipitated from an ammoniacal solution by a magnesium salt as white crystalline *ammonium magnesium phosphate*,  $\text{NH}_4\text{MgPO}_4 + 6\text{aq}$ . Another very characteristic test for phosphoric acid is that in nitric acid solution a finely crystalline, yellow precipitate is produced by ammonium molybdate,



especially on warming. This precipitate has approximately the composition  $14\text{MoO}_3 + (\text{NH}_4)_3\text{PO}_4 + 4\text{H}_2\text{O}$ , i. e. it is an ammonium phospho-molybdate. Precipitation in acid solution is of great advantage here, since most of the phosphates are soluble only in acids.

**PYROPHOSPHORIC ACID,  $\text{H}_4\text{P}_2\text{O}_7$ .**

147. One method of producing this acid was given in the preceding paragraph. In preparing it, it is more practicable, however, to heat the secondary sodium phosphate (the ordinary sodium phosphate of commerce), because in this case only one molecule of water can be driven off from two molecules of the salt:



After being heated the sodium pyrophosphate is dissolved in water and lead acetate is added to precipitate lead pyrophosphate, which is then decomposed with hydrogen sulphide.

Pyrophosphoric acid can be obtained from its solution as a colorless vitreous mass by evaporation in a vacuum at a low temperature. When dissolved in water of ordinary temperature, the acid remains unchanged for quite a while; on warming this solution, especially after the addition of a little mineral acid, it is converted into ortho-acid (§ 145).

All four hydrogen atoms are replaceable by metals; we should therefore expect to find four classes of salts. In reality only two are known,  $\text{M}_4\text{P}_2\text{O}_7$  and  $\text{M}_2\text{H}_2\text{P}_2\text{O}_7$ . The neutral, as well as the acid, alkali salts are soluble in water; the neutral salts of other bases are insoluble, the acid salts chiefly soluble.

Pyrophosphoric acid is distinguished from the ortho-acid by the fact that solutions of its salts give a *white* precipitate,  $\text{Ag}_4\text{P}_2\text{O}_7$ , with silver nitrate, and from the meta-acid by not coagulating white of egg and giving no precipitate with barium chloride.

**METAPHOSPHORIC ACID,  $\text{HPO}_3$ .**

148. This acid is obtained by heating the ortho- or the pyro-acid till no more water passes off, or by heating ammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$ . Moreover, on dissolving phosphorus pentoxide in cold water, the product is at first chiefly meta-acid.

At ordinary temperatures metaphosphoric acid is a vitreous solid (hence the name *glacial phosphoric acid*), which can be

melted and easily drawn out into threads. On being heated strongly it volatilizes without breaking up into water and pentoxide. When boiled in aqueous solution it goes over into orthophosphoric acid. It is very deliquescent; use is made of this property occasionally.

Metaphosphoric acid is monobasic, corresponding to the formula  $\text{HPO}_3$ . Its alkaline salts only are soluble in water. In solution the meta-acid can be distinguished from the ortho- and the pyro- by its ability to coagulate white of egg and give white precipitates with chlorides of barium or calcium.

There are salts of various acids known, which must be regarded as polymers of metaphosphoric acid, e.g.  $\text{K}_2\text{P}_2\text{O}_6$ , potassium di-metaphosphate; there exist also tri-, tetra- and hexa-metaphosphates, i.e. salts of the acids  $\text{H}_3\text{P}_3\text{O}_9$ ,  $\text{H}_4\text{P}_4\text{O}_{12}$ , and  $\text{H}_6\text{P}_6\text{O}_{18}$ .

#### Hypophosphoric Acid, $\text{H}_4\text{P}_2\text{O}_6$ .

149. If commercial stick phosphorus is exposed to a slow oxidation in moist air in the manner pictured in Fig. 47, so that each stick is supported

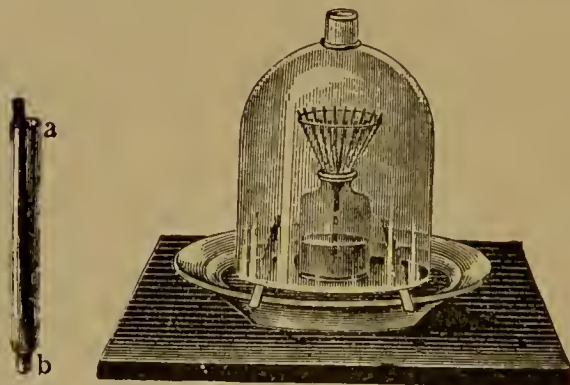
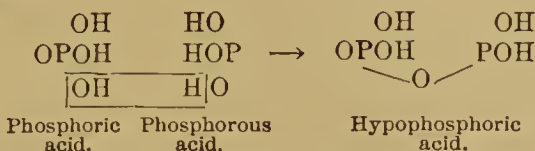


FIG. 47.—SLOW OXIDATION OF MOIST PHOSPHORUS.

in a tube *ab* by itself (on account of the danger of catching fire) and several such tubes rest on a funnel under a bell-jar standing in a dish of water, an acidic liquid is formed which contains phosphoric, phosphorous and hypophosphoric acids.

The last of the three can be eliminated by neutralizing the liquid with soda and evaporating. The almost insoluble acid sodium hypophosphate,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 + 6\text{H}_2\text{O}$ , is precipitated. If this salt is dissolved in water and barium chloride added, a precipitate of barium hypophosphate is formed, from which an aqueous solution of the free acid can be obtained by means of dilute sulphuric acid. This can be evaporated at  $30^\circ$  to a sirupy consistency without decomposition and, when left in a vacuum, yields crystals

of the acid. At an elevated temperature and in the presence of a mineral acid phosphorous and phosphoric acids are formed. This behavior justifies the consideration of hypophosphoric acid as a mixed anhydride of the two last-named acids :



This compound is also formed by the oxidation of phosphorus with the aid of copper sulphate solution (§ 134). Its silver salt is obtained by the oxidation of phosphorus with nitric acid in the presence of silver nitrate.

Hypophosphoric acid is tetrabasic, four classes of salts being known.

#### Metaphosphorous Acid, $\text{HPO}_2$ .

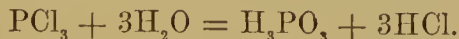
150. This compound was found by VAN DER STADT during the slow oxidation of phosphine under reduced pressure (§ 137) :



The sides of the vessel become covered with feather-like crystals of  $\text{HPO}_2$ . These melt at a much higher temperature than the crystals of phosphorous acid and are converted into the latter by the action of water vapor.

#### PHOSPHOROUS ACID, $\text{H}_3\text{PO}_3$ .

151. In § 149 it was mentioned that this acid is formed by the slow oxidation of phosphorus in moist air. It is more easily prepared by decomposing phosphorus trichloride with water :



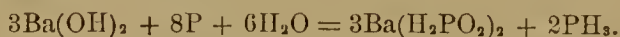
The hydrochloric acid can be expelled by evaporating at  $180^\circ$  and the phosphorous acid crystallizes out on cooling. Melting-point  $70.1^\circ$ . It is very hygroscopic. Heating decomposes it into phosphoric acid and phosphine. It has a strong reducing action, being itself oxidized to phosphoric acid. The oxygen of the air acts on it very slowly. It precipitates the metals from solutions of gold chloride, mercuric chloride, silver nitrate, etc. A characteristic reaction is the reduction of sulphur dioxide to sulphur, which takes place at ordinary temperatures, when solutions of the two substances are mixed.

In spite of its *three* hydrogen atoms, phosphorous acid acts as

a *dibasic* acid. As we have already observed, the ionization of polybasic acids sometimes affects only one H<sup>+</sup> ion at first, the others being split off with increasing difficulty. According to OSTWALD it may be supposed that ionization beyond 2H<sup>+</sup> and HPO<sub>3</sub>" is in this case so difficult that the acid seems to be only dibasic. The phosphites are not oxidized by the air, but are by the action of oxidizing-agents; e.g. they set the precious metals free from their salts, as does also the acid itself. Heating breaks them up into hydrogen, pyrophosphate and phosphide. The soluble phosphites give precipitates with baryta- or lime water.

#### Hypophosphorous Acid, H<sub>3</sub>PO<sub>2</sub>.

152. Salts of this acid are produced by heating phosphorus with caustic soda, lime-water or baryta-water (§ 136):



It can be set free from these salts by sulphuric acid; the aqueous solution is evaporated up to 140° and then cooled strongly, whereupon the acid crystallizes out. Melting-point, 17.4°. On being sufficiently heated it yields phosphine and phosphoric acid.

Hypophosphorous acid is a very strong reducing agent. Gold, silver and mercury are precipitated from solutions of their salts by the free acid as well as its salts. Sulphur dioxide is reduced to sulphur at ordinary temperatures. In these reactions the acid itself is converted into phosphoric acid. It is distinguished from phosphorous acid by its behavior towards copper sulphate solution; when it is warmed with the latter, a red precipitate of copper hydride, Cu<sub>2</sub>H<sub>2</sub>, is formed. Hypophosphorous acid is monobasic.

#### Compounds of Phosphorus and Sulphur.

153. Various compounds of this sort are known; all of them are obtained by warming the two elements together. As the reaction is very vigorous with yellow phosphorus, the red is usually employed.

The compound P<sub>2</sub>S<sub>6</sub>, which is of service in organic chemistry, is a yellow crystalline substance, melting at 274°–276° and boiling at 518°. On being warmed with water it yields phosphoric acid and sulphuretted hydrogen. P<sub>2</sub>S<sub>6</sub> unites with 3 molecules of K<sub>2</sub>S to form a *sulphophosphate*, K<sub>3</sub>PS<sub>4</sub>, i.e. a phosphate whose oxygen is replaced by sulphur.

Several compounds containing a halogen in addition to phosphorus and sulphur are known, e.g. PSCl<sub>5</sub>. This *phosphorus sulphochloride* can be prepared by treating phosphorus pentachloride with hydrogen sulphide, a method analogous to that of forming the oxychloride from the pentachloride

and water. A more convenient method is by the action of the pentachloride on the pentasulphide, which carries out the analogy to oxy-compounds still farther (§ 142):

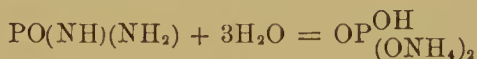


It is a colorless liquid, boiling at  $125^\circ$ ; it is decomposed by water into phosphoric acid, hydrochloric acid and hydrogen sulphide.

#### Compounds containing Phosphorus and Nitrogen.

154. The compounds of this class are also numerous. Among them are *amidophosphoric acid*,  $\text{OP}_{\text{NH}_2}^{\text{(OH)}_2}$ , and *diamidophosphoric acid*,  $\text{OP}_{(\text{NH}_2)_2}^{\text{OH}}$ . As their names indicate, these compounds behave like acids.

If dry ammonia is conducted over phosphorus pentachloride, a white mass is obtained which consists supposedly of ammonium chloride,  $\text{NH}_4\text{Cl}$ , and a compound  $\text{PCl}_3(\text{NH}_2)_2$ . With water it forms *phosphamide*,  $\text{PO}(\text{NH})(\text{NH}_2)$ , a white insoluble powder. On being boiled with water secondary ammonium phosphate is formed:



The name *phospham* is given to a compound  $\text{P}_3\text{H}_2\text{N}_6$ , which is formed from the product of the action of ammonia on phosphorus pentachloride, when it is heated in the absence of air till no more ammonium chloride fumes appear. It is insoluble in water. When fused with potassium hydrate, it breaks up as follows:



### ARSENIC.

155. Arsenic occurs in nature in the free state—native. More frequently it is found in combination with sulphur (*realgar*,  $\text{As}_2\text{S}_2$ , and *orpiment*,  $\text{As}_2\text{S}_3$ ) and with metals (*arsenopyrite*, or *mispickel*,  $\text{FeAsS}$ , and *cobaltite*,  $\text{CoAsS}$ ); also with oxygen as  $\text{As}_2\text{O}_3$  (*arsenolite*).

The extraction of the element from these minerals is simple. Arsenopyrite yields arsenic on mere heating, the latter subliming. Arsenolite is reduced with carbon:



*Physical Properties and Allotropic Conditions.*—The condition in which arsenic usually occurs is the crystalline. It then has a steel-gray color and a specific gravity of 5.727 at  $14^\circ$  and is a good

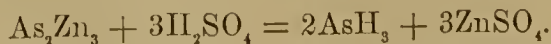
conductor of electricity. It sublimes under ordinary pressure without melting; under increased pressure, however, it melts at 500°. By sublimation in a current of hydrogen a second crystallized form can be obtained together with a black modification, which according to RETGERS is also crystallized. An amorphous modification results from the decomposition of hydrogen arsenide by heat, the arsenic appearing as a dark brown deposit on the sides of the glass. Finally there is a yellow modification which is formed when arsenic vapor is strongly cooled. It resembles yellow phosphorus very much, for it is soluble in carbon bisulphide, oxidizes quickly in the air with slight luminescence, and smells like garlic. It is very volatile and easily transformed into the black modification. At an elevated temperature (360°) all of them pass over into the ordinary crystalline form.

*Vapor Density.*—The lemon-yellow vapor of arsenic has a density of 10.2 (air = 1) at about 860°, which makes the molecular weight 293.8. At 1600°–1700° the vapor density is less by half, being 5.40. Since the atomic weight of arsenic is 75, its molecule therefore contains four atoms at about 860° and two at 1600°–1700°.

*Chemical Properties.*—Arsenic is not affected by dry air at ordinary temperatures; in moist air it becomes covered with a coating of oxide. At 180° it burns with a bluish flame to the oxide  $\text{As}_4\text{O}_6$ , giving off a peculiar garlic-like odor. At an elevated temperature it combines with many elements directly; it unites with chlorine without the aid of heat, producing scintillations.

#### HYDROGEN ARSENIDE. ARSINE, $\text{AsH}_3$ .

156. Direct synthesis from the elements is not possible with this compound. It is formed when almost any arsenic compound comes in contact with nascent hydrogen (zinc + sulphuric acid). When thus prepared it contains a good deal of hydrogen, however. Pure arsine is obtained by treating zinc arsenide or sodium arsenide with dilute sulphuric acid:



*Physical Properties.*—Hydrogen arsenide is a gas; it liquefies at  $-40^\circ$  but does not solidify as low as  $-110^\circ$ . Sp. g. = 38.9 (H = 1). It must be handled with great care, as it is very poison-

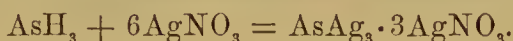
ous. Fortunately its presence can be easily detected by its peculiar, disagreeable odor.

*Chemical Properties.*—Arsine can be decomposed into its elements by heat. If the gas is passed through a hot glass tube, arsenic is deposited on the sides in the form of a metallic mirror. Induction sparks also decompose it. By the latter means it can be shown that the resulting volume of hydrogen is  $1\frac{1}{2}$  times as large as that of the gas itself, in accord with the formula  $\text{AsH}_3$ . It is an endothermic compound:



It has been made to explode by fulminating mercury (§ 119).

Hydrogen arsenide burns with a pale flame, yielding water and arsenious oxide,  $\text{As}_2\text{O}_3$ , if sufficient air is present; if such is not the case, or if the flame is cooled, arsenic is deposited. On heating potassium or sodium in the gas, an arsenide,  $\text{AsK}_3$  or  $\text{AsNa}_3$ , is formed. Hydrogen arsenide precipitates the yellow compound  $\text{AsAg}_3 \cdot 3\text{AgNO}_3$  from a very concentrated solution of silver nitrate:



This is decomposed by the addition of water into arsenious acid, nitric acid and metallic silver, the latter being deposited.

This reaction is called GUTZEIT'S *test*. It is usually made in the following way: A drop of 50%  $\text{AgNO}_3$  solution is placed on a piece of filter paper and the moist spot is held over a test-tube containing some zinc, dilute sulphuric acid and the substance to be tested for arsenic. If arsenic is present, the spot becomes yellow, and turns black when moistened with water.

*Composition of Arsine.*—If arsine is passed over hot copper oxide, water and copper arsenide are formed. The ratio of hydrogen to arsenic in arsine is determined from this reaction. For 1 part (by weight) of hydrogen 24.97 parts of arsenic are obtained. The molecular weight of the compound, as found from the specific gravity (see above), is 77.9; since the atomic weight of arsenic is 75, the formula of arsine must be  $\text{AsH}_3$ .

#### Detection of Arsenic.

157. The majority of arsenic compounds are very poisonous. Several of them are of practical use and hence are on the market, e.g. white arsenic,  $\text{As}_2\text{O}_3$  (rat-poison); orpiment,  $\text{As}_2\text{S}_3$ ; Schweinfurt green, or copper

arsenite. Poisonings with these substances happen occasionally. Some arsenic compounds, because of their pretty green color, are still used in dyeing tapestries, portières, and the like. Rooms in which these are hung usually contain particles of arsenical matter, which are injurious to the health. Further, a certain species of mould, *penicillium brevicaulis*, which is sometimes found in such tapestries, has the power of generating volatile and very poisonous arsenic compounds. The chemist is therefore quite frequently called upon to analyze a given sample (of dyed materials or the like, or the contents of a stomach) for arsenic. For this purpose a method has been devised which enables him to detect with certainty extremely small amounts of arsenic. It involves the following operations: The organic substance in question is at first disintegrated as well as possible, usually by digestion with hydrochloric acid on the water bath, a little potassium chlorate being added from time to time. Thus the arsenic com-

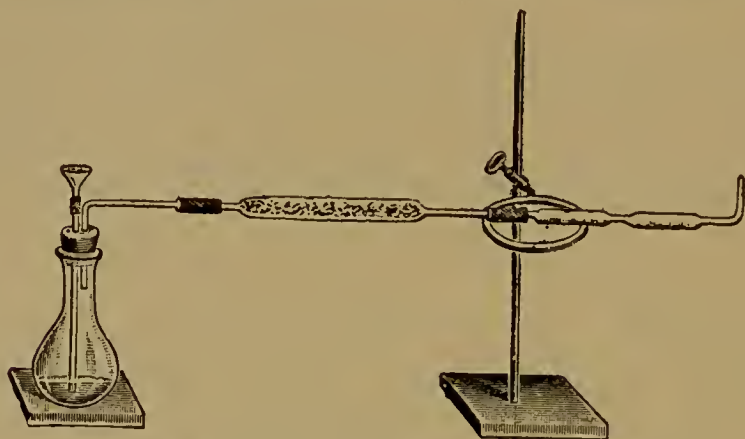


FIG. 48.—MARSH APPARATUS.

pound is oxidized to arsenic acid. When the chlorine has been expelled by warming and the liquid has been filtered, hydrogen sulphide is passed in for quite a while at a temperature of about  $80^{\circ}$  to precipitate the arsenic as sulphide. The sulphide is then dissolved in nitric acid (in case the presence of antimony is suspected, it must first be removed); this solution is evaporated to dryness to get rid of the excess of acid, the dry residue is dissolved in water, and this liquid then tested in the MARSH apparatus, one form of which is shown in Fig. 48.

This consists of a small flask, in which hydrogen is generated from zinc and sulphuric acid; the liquid to be investigated is poured down the funnel-tube; if arsenic is present, arsine is formed. The mixture of hydrogen and arsine is dried by calcium chloride in the wide tube and then enters a tube of hard glass, which is narrowed at several places and drawn to a point at the further end. As the gas leaves the narrowed end, which is bent upward, it is lighted. Thereupon the tube is heated



with a flame on the near side of a narrowed place. The arsine is broken up and arsenic is deposited as a bright metallic mirror in the narrowed part. From the extent and thickness of the deposit one can estimate the number of milligrams of arsenic present. If the hydrogen arsenide is not heated, it passes on to the flame and is burned. A cold porcelain dish held in the flame is soon coated with a deposit of arsenic, which is readily soluble in sodium hypochlorite solution (sodium arsenate being formed). This solubility enables us to distinguish arsenic from antimony.

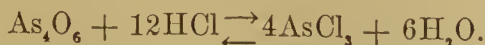
Arsenic is quite widely distributed, although in small amounts; hence we always have to reckon with the possibility of traces of it being present in the reagents and glass utensils of the laboratory. In order to test this a "blind experiment" is performed, i.e. all the operations are carried out with duplicate amounts of the required chemicals but without the addition of the substance to be analyzed. Not until the materials used are proven to be free from arsenic is it permissible to use them in an actual test.

Whether or not textile fabrics and the like have been dyed with Schweinfurt green (copper arsenite) can be determined easily by the GUTZEIT test. Another method is to use the above-mentioned penicillium brevicaulis. This is cultivated on bread which is soaked with the liquid to be tested for arsenic. The least trace of the latter reveals itself by a characteristic garlic-like odor, caused by the evolution of arsenical gases.

### Compounds of Arsenic with the Halogens.

158. Only two arsenic-halogen compounds of the type  $\text{AsX}_5$  are known, viz. the *penta-iodide*,  $\text{AsI}_5$ , and the *pentafluoride*,  $\text{AsF}_5$  (and the latter only in combination with potassium fluoride:  $\text{KF} \cdot \text{AsF}_5$ ). Aside from these only compounds of the type  $\text{AsX}_3$  are known.

**Arsenic trichloride**,  $\text{AsCl}_3$ , can be obtained by direct synthesis or by the action of hydrochloric acid on white arsenic. The latter way is analogous to the formation of metal chlorides from the oxide and hydrochloric acid. This compound is a colorless oily liquid having a specific gravity of 2.205 ( $d_4^\circ$ ). It freezes at  $-18^\circ$  and boils at  $130.2^\circ$ . It is extremely poisonous. When exposed to the air it throws off dense white fumes. With a little water it forms an oxychloride,  $\text{As}(\text{OH})_2\text{Cl}$ ; with much water hydrochloric acid and arsenious oxide. In this latter system a rise of temperature results in partial re-formation of the trichloride, which is volatile with the water vapor. The following equilibrium seems to exist:



## Oxygen Compounds of Arsenic.

Two such compounds are known:  $\text{As}_2\text{O}_3$ , *arsenious oxide*, and  $\text{As}_2\text{O}_5$ , *arsenic oxide*.

ARSENIUS OXIDE,  $\text{As}_2\text{O}_3$ .

159. Arsenious anhydride (commonly called "arsenic" or "white arsenic") is found in nature. It is formed by the combustion of arsenic in air or oxygen and by the oxidation of arsenic with dilute nitric acid. It is manufactured commercially by roasting arsenical ores; the oxide volatilizes and is condensed in brick-walled chambers, where it collects as a white powder ("arsenic meal"). It is refined by sublimation from iron cylinders.

*Physical Properties.*—Arsenious oxide is an odorless solid, that under ordinary pressure does not melt, but sublimes. Under higher pressure it is possible to melt it. At  $800^\circ$  its vapor density is 198 ( $O = 16$ ), which makes the molecular formula  $\text{As}_4\text{O}_6$ . Above this temperature dissociation begins and at  $1800^\circ$  the vapor density corresponds to the formula  $\text{As}_2\text{O}_3$ . By the ebulliscope method (elevation of the boiling-point) the molecular formula has been found to be  $\text{As}_4\text{O}_6$  at  $205^\circ$  also (in boiling nitrobenzene).

*Various Modifications.*—Arsenious oxide is known in a vitreous form as well as in crystals of the regular and monoclinic systems.

The vitreous modification is produced when the compound is sublimed or heated to the sublimation-point. Sp. g. = 3.738. After standing for some time at ordinary temperatures, this form becomes white like porcelain because of conversion into isometric crystals. The latter form is better obtained by dissolving the vitreous modification in water or hydrochloric acid and letting it crystallize out. During the crystallization the strange phenomenon of bright luminescence is observed. This luminescence does not appear when crystallized arsenious oxide is recrystallized. The transformation of the amorphous into the regular variety is accompanied by the evolution of heat (5.330 Cal.). The monoclinic form is obtained by conducting the crystallization above  $200^\circ$  instead of at ordinary temperatures. If the lower half of a sealed glass tube containing arsenious oxide be heated above  $400^\circ$ , it will be found after cooling that the lower heated part contains vitreous, the middle monoclinic, and the upper octahedral, arsenious oxide.

Since the transformation of amorphous into crystallized arsenious oxide takes place even at ordinary temperatures (rapidly at  $100^\circ$ ) and with the evolution of heat, the octahedral form is to be regarded as the stable one

at ordinary temperatures; the glassy form is only able to exist at these temperatures, because the velocity of transformation is then very small. According to the above, if octahedral arsenious oxide is gradually warmed, we have first a transformation into monoclinic and then another into amorphous. The transition-temperatures have not yet been determined.

*Chemical Properties.*—Arsenious oxide is easily reduced to arsenic; for example, by heating with charcoal or nascent hydrogen. It is also easily oxidized to arsenic oxide and is therefore useful as a reducing agent. This oxidation can be brought about by chlorine, bromine (bromine-water), iodine solution, potassium permanganate, strong nitric acid, etc. It is slightly soluble in water; the solution has a salty metallic taste and a weak acid reaction. In acids it dissolves much more easily, because it acts towards them as a basic oxide. It was stated above (§ 158) that a solution of the oxide in hydrochloric acid gives off arsenious chloride. White arsenic is a rank poison; freshly precipitated ferric hydrate serves as an antidote.

#### ARSENIC OXIDE, $(As_2O_5)_x$ .

160. This compound cannot be prepared like the corresponding phosphorus compound by burning arsenic in the air, for the oxidation goes no farther than to arsenious oxide. The higher oxide can only be prepared by heating arsenic acid in the air:



Arsenic anhydride is a white glassy substance, that dissolves in water slowly, going over into arsenic acid. By heating with carbon it is easily reduced to arsenic. At an elevated temperature it breaks up into oxygen and arsenious oxide. Its molecular weight is not known; the formula  $As_2O_5$  is simply empirical.

#### Oxyacids of Arsenic.

Two of these are known: *arsenious acid*,  $H_3AsO_3$ , (only in aqueous solution and salts) and *arsenic acid*,  $H_3AsO_4$ .

#### ARSENIOUS ACID, $H_3AsO_3$ .

161. This acid exists in the aqueous solution of the anhydride. On evaporation, however, the anhydride and not the acid separates out. This acid forms three classes of salts, according as one, two

or three of its hydrogen atoms are replaced by metals; it is therefore tribasic. Certain salts derive themselves from a *meta-arsenious acid*,  $\text{HAsO}_2$ .

The salts of the alkalis are soluble in water; those of the other metals are not, but dissolve easily in acids, however. A neutral arsenite-solution gives a yellow precipitate of silver arsenite,  $\text{Ag}_3\text{AsO}_3$ , with silver nitrate.

The solution of the free acid is easily oxidized to arsenic acid by iodine solution :



Such a solution can therefore also be employed for the titration of iodine (§ 93).

#### ARSENIC ACID, $\text{H}_3\text{AsO}_4$ .

162. This acid is most easily obtained by the oxidation of a solution of arsenious acid by warming it with nitric acid. On concentrating the solution the compound  $2\text{H}_3\text{AsO}_4 + \text{H}_2\text{O}$  separates out (below  $15^\circ$ ); this substance gives off its water of crystallization at  $100^\circ$  and yields *orthoarsenic acid*,  $\text{H}_3\text{AsO}_4$ , which crystallizes in fine needles. When heated more it gives off water (at  $180^\circ$ ) and goes over into *pyroarsenic acid*,  $\text{H}_4\text{As}_2\text{O}_7$ , which separates in the form of hard glistening crystals. On being heated still higher the latter compound gives up another molecule of water, the final product being white crystalline *meta-arsenic acid*,  $\text{HAsO}_3$ . This conduct is completely analogous to that of phosphoric acid; however, metaphosphoric cannot be converted into the anhydride by heat as can arsenic acid (§ 160). The pyro- and meta-arsenic acids are stable only in the solid state; when treated with water they are converted into the ortho acid, the transformation being much quicker than with the corresponding phosphorus acids.

Orthoarsenic acid is easily soluble in water. Its salts, the arsenates, exist in three classes; of the tertiary only those of the alkalis are soluble in water. The reactions of arsenic acid are very similar to those of phosphoric acid (§ 146); in this case also a mixture of ammonia, ammonium chloride and magnesium sulphate (*magnesia mixture*) precipitates a white crystalline ammonium magnesium salt,  $\text{Mg}(\text{NH}_4)\text{AsO}_4 + 6\text{H}_2\text{O}$ . Ammonium molybdate produces a yellow finely crystalline precipitate, whose composition and appearance correspond to those of the phosphorus compound.

The precipitates formed with silver nitrate are, however, unlike in color:  $\text{Ag}_3\text{PO}_4$  is yellow,  $\text{Ag}_3\text{AsO}_4$  reddish brown.

### Sulphur Compounds of Arsenic.

163. Three are known: *arsenic disulphide (realgar)*,  $\text{As}_2\text{S}_2$ ; *arsenic trisulphide (orpiment)*,  $\text{As}_2\text{S}_3$ ; *arsenic pentasulphide*,  $\text{As}_2\text{S}_5$ .

#### Arsenic disulphide, $\text{As}_2\text{S}_2$ ,

occurs in nature as realgar (§ 155). It forms beautiful ruby-red crystals of a specific gravity of 3.5. It is used as a pigment. It is manufactured artificially by fusing sulphur and arsenic together; the resulting products vary in composition, however.

#### ARSENIC TRISULPHIDE, $\text{As}_2\text{S}_3$ .

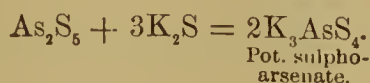
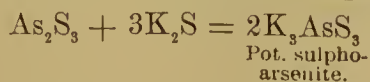
Arsenic is precipitated from the acid solution of arsenious oxide by sulphuretted hydrogen as sulphide; in this respect too it behaves as a heavy metal. In the above reaction arsenic trisulphide is deposited as an amorphous yellow powder. The latter occurs in nature as *orpiment* (§ 155), having a laminated crystalline structure; it owes its name to its beautiful golden lustre. By fusing artificial arsenic trisulphide a product is obtained, which is very similar to the natural orpiment, but has a lower specific gravity (2.7 instead of 3.4). Commercially the trisulphide is prepared by fusing white arsenic with sulphur; the product still contains the oxide, however, and is therefore poisonous. Arsenic trisulphide is insoluble in water and in acids.

#### ARSENIC PENTASULPHIDE, $\text{As}_2\text{S}_5$ .

After sulphuretted hydrogen has been led into a warm acidulated solution of arsenic acid for some time, arsenic is precipitated as an amorphous yellow powder of the composition  $\text{As}_2\text{S}_5$ . The latter is also obtained by fusing arsenic trisulphide with the required amount of sulphur. In the absence of air it can be sublimed without decomposition. It is insoluble in water and in alkalies.

#### SULPHO-SALTS OF ARSENIC.

164. The trisulphide and the pentasulphide of arsenic dissolve easily in alkali sulphides, forming salts of *sulpho-acids*:

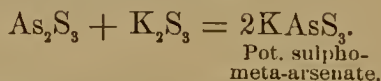


The formation of these sulpho-salts can be regarded as parallel to that of an oxy-salt from a basic oxide and an acid anhydride, e. g. :



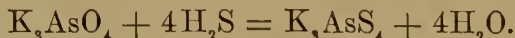
The trisulphide and the pentasulphide are therefore to be considered as *sulpho-anhydrides* of those sulpho-acids.

The sulpho-arsenates can also be obtained from arsenic trisulphide with the aid of an alkali polysulphide:



This reaction can be explained by supposing that the arsenic trisulphide is converted into the pentasulphide by the excess of sulphur, just as the trioxide is oxidized to the pentoxide.

They are also produced by treating an arsenate with hydrogen sulphide:

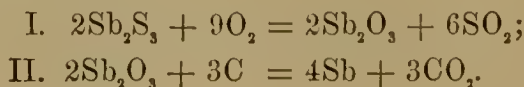


The sulpho-arsenites and sulpho-arsenates of the alkalies dissolve easily in water and can be obtained in the crystalline form from the solution; those of the other metals are insoluble. The free sulpho-acids are unknown. On the addition of an acid to the solution of a sulpho-salt, the liberated sulpho-acid breaks up into hydrogen sulphide and arsenic tri- or pentasulphide.

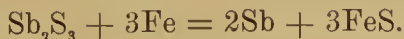
### ANTIMONY.

165. Antimony occurs in nature in *stibnite*,  $\text{Sb}_2\text{S}_3$ , as well as in many less common minerals. Stibnite was known to the ancients. In Japan it is found in magnificent large crystals. Antimony was frequently employed by the alchemists. BASILIUS VALENTINUS at the beginning of the seventeenth century described its extraction from stibnite in a monograph entitled "The triumphal car of Antimonium."

The element is at present obtained from stibnite by two processes. In one the mineral is roasted, being thus transformed into antimonious oxide. This oxide is then reduced with charcoal to metallic antimony:



The other method is to fuse the mineral with iron:



This crude antimony usually still contains arsenic, lead, sulphur, etc. It can be refined by fusing with a little saltpetre, the impurities being oxidized.

*Physical Properties.*—Antimony is silvery white and has a high metallic lustre and a laminate-crystalline structure (rhombohedral); as a result of the latter it is very brittle and can be easily pulverized. Sp. g. = 6.71–6.86. Melting-point  $432^\circ$ ; boiling-point  $1450^\circ$ . MENSCHING and V. MEYER succeeded in determining the vapor density at  $1437^\circ$ , i.e. slightly below the boiling-point, and found that the molecule, unlike that of phosphorus or arsenic, consists of less than four atoms.

*Chemical Properties.*—At ordinary temperatures the element is not affected by the air; when heated, it burns with a bluish-white flame to the trioxide. It combines with the halogens directly, producing scintillations (§ 27). It is dissolved by hydrochloric acid, although very slowly, with the evolution of hydrogen, thus asserting its metallic character. Aqua regia dissolves it readily.

*Uses.*—Antimony is a constituent of various alloys. The most important of these is type-metal, from which printer's type is made. It contains lead (50%), antimony (25%) and tin (25%). The composition is often different from this, however.

#### HYDROGEN ANTIMONIDE, STIBINE, $\text{SbH}_3$ .

166. Stibine is formed when nascent hydrogen acts on a soluble antimony compound. It is best prepared by treating an alloy of zinc and antimony with dilute hydrochloric acid. This method, like all others, yields a product containing a large admixture of hydrogen. If this gas mixture is passed through a U-tube and the whole is plunged in liquid air, stibine condenses to a white solid mass, that soon melts after the tube is removed from the liquid air. It vaporizes to a relatively stable gas. The least trace of oxygen, however, causes some antimony to be deposited.

If an electric spark is passed through stibine gas it explodes, antimony is set free and the volume of hydrogen liberated is found, in accord with the formula  $\text{SbH}_3$ , to be  $1\frac{1}{2}$  times that of the

stibine. It is also decomposed easily by heating the vessel containing it with a Bunsen burner.

Stibine has a characteristic musty odor, quite unlike that of phosphine or arsine.

When the mixture of hydrogen and stibine evolved from zinc-antimony is heated, as in the MARSII experiment (§ 157), it produces a metallic mirror and, when ignited, the flame gives a spot on cold porcelain analogous to that of arsenic. This metallic coating is distinguished from that of arsenic by a darker color, insolubility in hypochlorite solution and less volatility when heated in a current of hydrogen. Stibine precipitates a black powder from silver solution, consisting of a mixture of silver and silver-antimonide,  $\text{Ag}_3\text{Sb}$ .

### Halogen Compounds of Antimony.

167. Two compounds of this element with chlorine are known:  $\text{SbCl}_3$  and  $\text{SbCl}_5$ .

**Antimony trichloride**,  $\text{SbCl}_3$ , is obtained by treating antimony sulphide or oxide with concentrated hydrochloric acid. It forms a colorless laminar-crystalline mass, which is so soft that it was formerly known as "antimony butter" (*butyrum antimonii*). Its melting-point is  $73.5^\circ$  and its boiling-point  $223.5^\circ$ ; its vapor density 7.8 (air = 1) makes the formula  $\text{SbCl}_3$ .

It dissolves in water containing hydrochloric acid. Water decomposes it, forming oxychlorides. The composition of the oxychloride depends on the amount and the temperature of the water used in the decomposition. If 1 part by weight of trichloride is mixed with 1.7 parts of water, a precipitate is formed, that becomes crystalline in the course of time and has the composition  $\text{SbOCl}$ . If 5-50 parts of water at ordinary temperature are used to 1 part of trichloride, the oxychloride  $\text{Sb}_4\text{O}_5\text{Cl}_2$  (=  $2\text{SbOCl}$ ,  $\text{Sb}_2\text{O}_3$ ) is obtained, which gradually becomes crystalline on standing. The precipitates on being repeatedly boiled with water lose all their chlorine in the end and go over into the trioxide,  $\text{Sb}_2\text{O}_3$ .

These precipitates of oxychlorides, produced by water, are called *powder of Algaroth* and were once used as medicine.

**Antimony pentachloride**,  $\text{SbCl}_5$ , is prepared by heating antimony in a current of chlorine or treating fused trichloride with chlorine. It is a yellow, fuming, ill-smelling liquid, which



crystallizes at  $-6^{\circ}$ . When heated it dissociates into  $\text{SbCl}_3$  and  $\text{Cl}_2$ . It unites with water, forming  $\text{SbCl}_3 \cdot \text{H}_2\text{O}$  and  $\text{SbCl}_3 \cdot 4\text{H}_2\text{O}$ . Hot water decomposes it into hydrochloric and pyroantimonic acids.

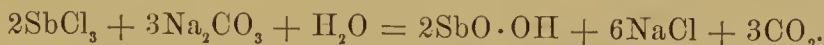
### Oxygen Compounds of Antimony.

168. Three are known: *antimony trioxide*,  $\text{Sb}_2\text{O}_3$ , *antimony tetroxide*,  $\text{Sb}_2\text{O}_4$ , and *antimony pentoxide*,  $\text{Sb}_2\text{O}_5$ .

**Antimony trioxide** occurs as a mineral, *senarmonite*. It can be obtained by burning antimony in the air, as well as by the oxidation of antimony with dilute nitric acid. It is dimorphic, occurring in both regular and rhombic crystals.

It is a light yellow crystalline powder, almost insoluble in water. It volatilizes at  $1560^{\circ}$ ; the vapor density at this temperature corresponds to the formula  $\text{Sb}_4\text{O}_6$ . It is insoluble in sulphuric and nitric acids but easily soluble in hydrochloric and tartaric acids and in alkalies. On being heated in the air it turns to the tetroxide.

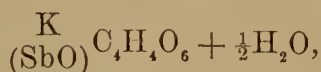
The corresponding hydroxide is  $\text{Sb}(\text{OH})_3$ . This hydrate separates out when tartar emetic (see below) is decomposed with dilute sulphuric acid. It gives up one molecule of water readily and passes over into the hydrate  $\text{SbO} \cdot \text{OH}$ , *meta-antimonious acid*. The latter is more easily obtained by treating a solution of the trichloride with soda solution:



It appears as a white precipitate, which is converted into antimonious oxide by boiling with water. This meta-antimonious acid is dissolved by alkalies, forming salts of the acid. One of them which has been obtained crystallized is the sodium meta-antimonite,  $\text{NaSbO}_2 + 3\text{H}_2\text{O}$ . The latter is difficultly soluble in water, and decomposes on concentration of its solution.

On the other hand antimony hydroxide displays basic properties by uniting with acids to form salts. There are salts known of  $\text{Sb}(\text{OH})_3$ , as well as of  $\text{SbO} \cdot \text{OH}$ . Examples of the former kind are the crystallized *antimony sulphate*,  $\text{Sb}_2(\text{SO}_4)_3$ , and the nitrate,  $\text{Sb}(\text{NO}_3)_3$ . As is the case with other trivalent metals, double salts are known, e.g.  $\text{KSb}(\text{SO}_4)_2$ . As to the salts derived from  $\text{SbO} \cdot \text{OH}$ , we may look at the group  $\text{SbO}$  as taking the place of a univalent

metal. Thus  $\text{SbO} \cdot \text{OH}$  may be compared with  $\text{KOH}$ . For this reason the group  $(\text{SbO})$  has been given the name *antimonyl*; one of its salts is *antimonyl sulphate*,  $(\text{SbO})_2\text{SO}_4$ . The most familiar antimonyl compound is *tartar emetic*, potassium antimonyl tartrate,



which is employed in medicine. It is prepared by boiling acid potassium tartrate (*cream of tartar*) with antimony oxide and water; tartar emetic is readily soluble in water.

#### ANTIMONY PENTOXIDE AND ANTIMONIC ACID.

**Antimonic acid**,  $\text{H}_3\text{SbO}_4$ , is obtained by warming antimony with concentrated nitric acid and also by decomposing the pentachloride with water. It is a white powder, almost insoluble in water and nitric acid; nevertheless when moist it turns litmus paper red. On heating saltpetre with powdered antimony the potassium salt of *meta-antimonic acid*,  $\text{KSbO}_3$ , is formed in an explosive reaction. When this is boiled with water it dissolves, producing *monopotassium orthoantimoniate*,  $\text{KH}_2\text{SbO}_4$ ; on fusing with potash *potassium pyroantimoniate*,  $\text{K}_4\text{Sb}_2\text{O}_7$ , is formed, which dissolves in water to  $2\text{KOH}$  and  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$ . In the case of antimony, as in that of phosphorus, we meet with three kinds of acids belonging to the highest stage of oxidation; their formulæ correspond to those of the analogous phosphorus compounds.

**Antimony pentoxide**,  $\text{Sb}_2\text{O}_5$  (molecular weight unknown), can be obtained by heating antimonic acid at  $300^\circ$ . It is a yellow amorphous powder, soluble in hydrochloric acid. If heated strongly it gives up part of its oxygen and goes over into **antimony tetroxide**,  $\text{Sb}_2\text{O}_4$ , a white powder that turns yellow on heating but resumes its original color on cooling. This tetroxide can be regarded as *antimonyl meta-antimoniate*,  $\text{SbO}_3 \cdot \text{SbO}$ .

#### Sulphur Compounds of Antimony.

**169. Antimony trisulphide**,  $\text{Sb}_2\text{S}_3$ , is found in nature (§ 165). It can be made by leading hydrogen sulphide into a hydrochloric acid solution of the trichloride, from which it is deposited as an amorphous red powder. It can be melted; on cooling it crystallizes and takes on the appearance of stibnite.

An oxygen compound,  $\text{Sb}_2\text{S}_2\text{O}$ , occurs in nature as *kermesite*, or *red antimony*. A compound of supposedly the same composition is obtained by warming a solution of the trichloride with sodium thiosulphate; the preparation thus obtained bears the name *kermes* in pharmacy and *antimony vermilion* as a pigment.

**Antimony pentasulphide**,  $\text{Sb}_2\text{S}_5$ , is precipitated when hydrogen sulphide is passed into the acidified solution of antimonic acid. It is more easily obtained by the decomposition of sodium sulphantimoniate with dilute sulphuric acid. It forms an amorphous orange-red powder, which splits up into sulphur and trisulphide on being heated strongly. It is insoluble in dilute acids; boiling-hot concentrated hydrochloric acid dissolves it, forming antimony trichloride, hydrogen sulphide and sulphur. In aqueous solutions of alkalis and their sulphides it dissolves easily with the formation of sulphantimoniate,  $\text{M}_3\text{SbS}_4$ . The best known of these is *sodium sulphantimoniate*,  $\text{Na}_3\text{SbS}_4 + 9\text{H}_2\text{O}$  ("SCHLIPPE'S salt"). It can be obtained by boiling antimony trisulphide with sulphur and caustic soda solution. It crystallizes in large colorless tetrahedrons, is easily soluble in water (1 part by weight in 2.9 parts water at  $15^\circ$ ) and reacts alkaline. It is decomposed by acids, depositing pentasulphide; even carbonic acid causes this, hence the crystals become covered with a yellowish-red coating of pentasulphide after having stood some time in the air. The free sulphantimonic acid is not known.

## BISMUTH.

**170.** This element belongs undoubtedly among the metals, so far as its physical character is concerned; its chemical properties also class it with them in almost every respect, inasmuch as its oxides are mainly basic in their behavior.

It is found chiefly in the native state; but a sulphide,  $\text{Bi}_2\text{S}_3$ , *bismuth glance*, and a telluride, *tetradymite*, also occur in nature. Bismuth is obtained from the latter by roasting to the oxide  $\text{Bi}_2\text{O}_3$  and reducing with charcoal. The native metal is usually very pure. If refining is necessary, the fused metal is allowed to flow over a hot, somewhat inclined iron plate, so that the impurities are oxidized. The amount of bismuth in nature is not very great.

*Physical Properties.*—Bismuth is externally very similar to antimony; it is crystallized and very brittle and has a metallic

lustre, but differs from antimony in having a reddish-white color. Sp. g. = 9.823. It melts at  $286.3^{\circ}$  and boils above  $1090^{\circ}$ . It can be distilled in a current of hydrogen.

*Chemical Properties.*—At ordinary temperatures bismuth is unaffected by the air. On being heated it turns to the trioxide. It combines with the halogens directly. It is not attacked by hydrochloric or sulphuric acid at ordinary temperatures, but nitric acid dissolves it readily to form the nitrate. On being heated with sulphuric acid, it gives off sulphurous oxide and forms the sulphate. No hydrogen compound of bismuth is known.

Bismuth is employed in the manufacture of easily fusible alloys such as are used in making casts of woodcuts, stereotypes, etc. The most common of these alloys are NEWTON'S metal (8 bismuth, 5 lead, 3 tin; melting-point  $94.5^{\circ}$ ), ROSE'S metal (2 bismuth, 1 lead, 1 tin; melting-point  $93.75^{\circ}$ ) and WOOD'S metal (4 bismuth, 2 lead, 1 tin, 1 cadmium; melting-point  $60.5^{\circ}$ ).

### Halogen Compounds.

171. Compounds of the type  $\text{BiX}_3$  only are known. **Bismuth chloride**,  $\text{BiCl}_3$ , is formed by direct synthesis from the elements but more easily by dissolving bismuth in aqua regia. It is white and crystallized. Its melting-point is between  $225^{\circ}$  and  $230^{\circ}$  and its boiling-point at  $435^{\circ}$ . Its vapor density, 11.35 (air = 1), gives it the formula  $\text{BiCl}_3$ . If dissolved in a little water it forms a sirupy liquid; an excess of water gives **bismuth oxychloride**,  $\text{BiOCl}$ , and hydrochloric acid. This oxychloride is a white powder, insoluble in water but soluble in acids.

### Oxygen Compounds.

172. Four oxides are known:  $\text{BiO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{BiO}_2$  and  $\text{Bi}_2\text{O}_5$ .

**Bismuthous oxide**,  $\text{BiO}$ , is obtained by adding an alkaline stannous chloride solution to a solution of bismuth chloride. It is deposited as a dark-brown precipitate of  $\text{BiO}$ . When heated in the air it smolders like tinder. It is doubtful whether this precipitate is a homogeneous substance.

**Bismuth trioxide**,  $\text{Bi}_2\text{O}_3$ , is the most familiar oxide of this element. It has strictly basic properties. In order to prepare it we can heat the nitrate or carbonate or we can precipitate the hydroxide from the solution of a bismuth salt by means of a base.

and heat the precipitate. If a boiling solution of a bismuth salt is treated with caustic potash, the trioxide separates out in glistening needles of microscopic dimensions. Like the corresponding oxides of arsenic and antimony, it is dimorphic.

**Bismuth dioxide**,  $\text{BiO}_2$ , has been little studied; it is a reddish-yellow powder.

**Bismuth pentoxide**,  $\text{Bi}_2\text{O}_5$ , is obtained by heating bismuthic acid (§ 173) to  $130^\circ$ . It is a brown powder, that is very unstable and gives up oxygen when heated or when warmed with sulphuric acid. It does not form the corresponding pentachloride,  $\text{BiCl}_5$ , with hydrochloric acid, but gives free chlorine and the trichloride.

### Hydroxides and Salts.

**173. Bismuth hydroxide**,  $\text{Bi}(\text{OH})_3$ , is obtained by precipitating a bismuth salt with an alkali. It is an amorphous white powder, insoluble in potassium hydrate or ammonia. At  $100^\circ$  it goes over into the compound  $\text{BiO}\cdot\text{OH}$  with the loss of a molecule of water. Both of these hydroxides are wholly basic in character. The salts derived from  $\text{Bi}(\text{OH})_3$  are called neutral, those from  $\text{BiO}\cdot\text{OH}$  basic.

The *neutral nitrate*,  $\text{Bi}(\text{NO}_3)_3$ , is obtained by dissolving bismuth in nitric acid. It crystallizes with five molecules of water in large translucent triclinic prisms. It is deliquescent. The addition of much water converts it to the *basic nitrate*. A great excess of water produces  $\text{BiO}\cdot\text{NO}_3 + \text{BiO}\cdot\text{OH}$ , **bismuth subnitrate**, which is used in medicine.

**Bismuth sulphate**,  $\text{Bi}_2(\text{SO}_4)_3$ , is obtained as an amorphous white substance when the metal is heated with concentrated sulphuric acid. With water it forms a basic sulphate  $\text{Bi}_2(\text{OH})_4\text{SO}_4$ .

The potassium salt of **bismuthic acid**,  $\text{KBiO}_3$ , is obtained when an almost boiling-hot solution of potassium hydrate (sp. g. 1.43) and potassium chloride, in which bismuth trioxide is suspended, is electrolyzed. A dark red deposit separates out on the sides of the platinum dish (anode), having the above composition. By boiling it for a very short time with concentrated nitric acid, the scarlet bismuthic acid is produced. At  $100^\circ$ – $120^\circ$  the acid loses its hydrate water and the color turns from red to brown and finally to black, oxygen being gradually given off. If heated higher carefully, the entire mass turns deep brick-red suddenly at about  $300^\circ$ . This is an isomeric modification of the ordinary trioxide,  $\text{Bi}_2\text{O}_3$ .  $\text{Bi}_2\text{O}_4$  (i.e.  $2\text{BiO}_2$ ) can be considered as a basic bismuth salt of this acid;  $\text{BiO}\cdot\text{BiO}_3$ .

## Sulphur Compounds.

**174. Bismuth trisulphide** is found in nature (§ 170); artificially it can be prepared by heating bismuth with sulphur or by leading hydrogen sulphide into the aqueous solution of a bismuth salt. In the latter case it comes down as an amorphous black powder, that is easily soluble in warm dilute nitric acid. It is insoluble in alkalies and their sulphides, hence forms no sulpho-salts. When heated with an alkali sulphide solution to  $200^{\circ}$  it takes on a crystalline form similar to that of the natural mineral.

There is also a compound  $\text{Bi}_2\text{S}_2$ . It is obtained in gray needle-like crystals by fusing the elements together in the ratio of their atomic weights and suddenly cooling.

## SUMMARY OF THE NITROGEN GROUP.

**175.** Like the halogens and the elements of the oxygen group, the elements just discussed, viz. nitrogen, phosphorus, arsenic, antimony and bismuth, also form a natural group. Their family relation shows itself even in the formula-types of their compounds. The hydrogen compounds have the type  $\text{RH}_3$  (lacking with bismuth), the halogen compounds  $\text{RX}_3$  and  $\text{RX}_5$  (the latter also lacking with bismuth), the oxygen compounds  $\text{R}_2\text{O}_3$  and  $\text{R}_2\text{O}_5$ . In other words the elements of this group are trivalent or pentivalent. We find here, just as in the groups previously studied, that, as the atomic weight increases, a gradual change occurs in the physical properties, as the following small table shows:

	N.	P.	As.	Sb.	Bi.
Atomic weight.....	14.04	31.0	75	120	208.5
Spec. gravity..... (Water = 1)	0.885 liquid	1.8-2.1	4.7-5.7	6.7	9.8
Melting-point.....	.....	+ 44.4°	ca. 500°	+ 430°	+ 268°
Boiling-point.....	- 194.4°	+ 278°	.....	at white heat	
Color.....	colorless	yellow or red	gray	white	pink

In the chemical properties, also, regular variations are to be observed, all of which can be summed up in the general statement that the metalloïd character approaches the metallic as the atomic weight increases. Nitrogen forms either indifferent or acid-forming oxides only; so does phosphorus; arsenic, on the contrary,

displays a very weak basic character in arsenious oxide, since this oxide forms the trichloride with hydrochloric acid, the trichloride reacting inversely with water, however, and breaking up into hydrochloric acid and arsenious oxide. In antimony trioxide this basic character is a little stronger; some salts and double salts of it with acids are known. The corresponding chloride does not suffer an immediate hydrolytic dissociation with water, but oxychlorides are formed, which require a great deal of water to convert them entirely to the trioxide. While the highest oxides of arsenic and antimony have strictly acid properties, with bismuth the acidic nature has practically disappeared; the oxide  $\text{Bi}_2\text{O}_3$  has exclusively basic properties and  $\text{Bi}_2\text{O}_5$  acts like a peroxide, giving off oxygen readily (it yields chlorine with hydrochloric acid) and going over into  $\text{Bi}_2\text{O}_3$ .  $\text{BiCl}_3$  gives  $\text{BiOCl}$  with water and this is not decomposed by an excess of water.

In the hydrogen compounds, too, the gradual change of the properties is very plain. Consider the stability:  $\text{NH}_3$  requires very great heat to decompose it;  $\text{PH}_3$  and  $\text{AsH}_3$  a much lower temperature;  $\text{SbH}_3$  is unstable at ordinary temperatures when it comes in contact with oxygen, and the hydrogen compound of bismuth is so unstable that the conditions for its formation and existence have not yet been able to be ascertained. A similar change is noticeable in their ability to form  $\text{XH}_4$  ions in aqueous solutions; it is strong in  $\text{NH}_3$ , much weaker in  $\text{PH}_3$  and wholly absent with arsenic and antimony.

In the sulphur compounds a progressive change of color is observed.  $\text{P}_2\text{S}_5$  is bright yellow,  $\text{As}_2\text{S}_5$  deep yellow,  $\text{Sb}_2\text{S}_5$  red and  $\text{Bi}_2\text{S}_5$  black. The three first named are sulpho-anhydrides of sulpho-acids (§ 164); bismuth sulphide, however, is not, thus displaying again the more basic nature of bismuth.

## CARBON.

176. Carbon occurs in nature both free and combined. In combination it is found in large quantities in the salts of carbonic acid, above all in calcium carbonate, *limestone*, which sometimes forms great mountains. Farther, carbon is one of the elements of which animals and plants are composed. In these it is found in numerous compounds. Still larger is the number of artificially

prepared carbon compounds. The compounds of carbon exceed in number all other compounds together. For this reason and because of the peculiarities of the carbon compounds it is customary to treat them by themselves, as "organic chemistry." However, that we may be able to obtain a general survey of the elements, it is deemed advisable to discuss certain compounds of carbon in inorganic chemistry as well.

### Allotropic Forms of Carbon.

We know of three: *diamond*, *graphite* and *amorphous carbon*.

(a) **Diamond.**—LAVOISIER proved that this mineral consists of carbon.

As early as the seventeenth century ANSELMUS DE BOOT and NEWTON suspected that the diamond must be capable of burning because of its strong refractive power; not, however, until the year 1694 were experiments on this point undertaken. At the instigation of COSMUS III., Grand Duke of Tuscany, AVERANI and TARGIONI, members of the Academia del Cimento at Florence, then discovered that a diamond would burn in the focus of a concave mirror. Subsequently FRANÇOIS ETIENNE DE LORRAINE found that it also burns in a blacksmith's forge. As the diamond was then almost universally regarded as a very pure sort of quartz, these observations were little heeded. In the years 1766–1772, however, experiments were again instituted with wonderful care and precision by numerous French scholars in co-operation (among them D'ARCET, ROUELLE, CADET, MACQUER and LAVOISIER), to whom the leading Parisian jewelers at first furnished diamonds without cost. Their investigations revealed that diamond when heated away from air remains unchanged, but burns on the admission of air. Later LAVOISIER showed that carbon dioxide is formed from this combustion, and in 1814 DAVY proved that, when diamond burns, nothing else than this gas is formed, so that diamond must be pure carbon. Further, it was found by KRAUSE in 1890 that, when the carbon dioxide given off by the combustion of diamond is absorbed by caustic soda, a soda is produced which is in every respect identical with ordinary soda. Finally it has been possible to manufacture diamonds from amorphous carbon (see below).

The diamond crystallizes regular. Usually it is colorless, but yellow and black diamonds are also known; the black ones are called *carbonado*. The specific gravity of diamond is 3.50–3.55. It is a poor conductor of heat and electricity. The refractive index is very high:  $n = 2.42$ . The diamond is so hard that it scratches all other minerals. If diamond is subjected to a very



high temperature in the absence of air, it gradually turns to graphite. It resists the action of the strongest oxidizing agents, e.g. a mixture of nitric acid and potassium chlorate.

In 1893 MOISSAN succeeded in making diamonds artificially, although they were very small, the largest being about 0.5 mm. in diameter. His method consists essentially in dissolving carbon in molten iron at a high temperature and then letting it crystallize out under high pressure. If this pressure is not applied, the carbon crystallizes in the form of graphite. The higher the temperature of the molten iron, the more carbon it is able to dissolve. MOISSAN observed this for temperatures between  $1100^{\circ}$  and  $3000^{\circ}$ .

The process by which the artificial preparation of the diamond was carried out by MOISSAN is as follows: Iron is brought in contact with pure carbon (sugar charcoal) in the electric furnace

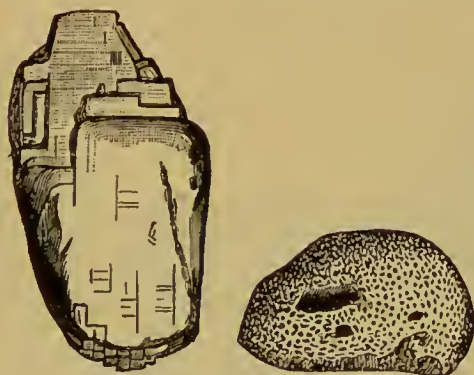


FIG. 49.—ARTIFICIAL DIAMONDS (MAGNIF.).

at a high temperature. After the iron has become saturated with carbon, the fused mass is suddenly cooled by pouring it into a hole drilled in a copper block, which is kept cold by water, and at once covering the cavity with an iron stopper. Thus a crust of solid iron forms on the outside of the molten mass and, since carbonaceous iron expands on solidifying, the inner portion will attempt to expand as it cools and thus generate an enormous internal pressure. When the iron is all cold, it is dissolved away by acids, leaving the carbon which did not combine with the iron. This residual carbon consists partly of small diamonds, which are identical with the natural diamond in hardness, crystal form, etc. Fig. 49 presents an enlarged view of some artificial specimens; they

display the same properties as the rough natural diamonds, particularly the rounded edges and angles and the striations.

The electric furnace that MOISSAN used for these and numerous other experiments is very simple in construction. It consists of two blocks of unslaked lime that fit tightly together. In the lower block there is a



FIG. 50.—MOISSAN'S ELECTRIC FURNACE (CROSS-SECTION).

trough in which the carbon terminals are laid. The upper block is slightly hollowed out on its lower side so as to reflect the heat rays on to the crucible. Fig. 50 shows a cross-section of an electric furnace, Fig. 51 a picture of the same apparatus in operation.

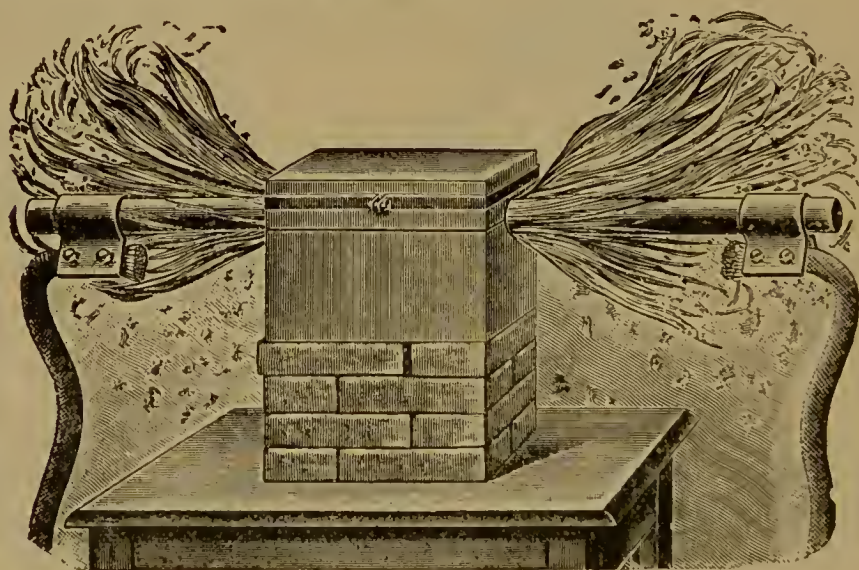


FIG. 51.—MOISSAN'S ELECTRIC FURNACE IN OPERATION.

The temperatures obtained in the electric furnace are as follows:

Current of	30 ampères	and	55 volts	with a steam-engine of	4 H.P.,	2250°
"	" 100	"	" 45	" " " "	" 8	2500°
"	" 450	"	" 70	" " " "	" 50	3000°

The last-named temperature can however only be maintained for a brief period, as the unslaked lime soon melts and flows like water. At 2500° the lime becomes crystalline in structure after a few minutes.

(b) **Graphite** is also crystallized carbon. Unlike diamond, it is very soft and opaque and a good conductor of heat and electricity. Sp. g. = 2.09–2.23. As was stated above, graphite can be prepared artificially by the crystallization of carbon from molten iron and by heating diamond strongly. There are various kinds of graphite. If graphite is treated with a mixture of perfectly dry potassium chlorate and very concentrated nitric acid, it turns to a yellow crystallized substance containing hydrogen and oxygen in addition to carbon and called *graphitic acid*. This substance is peculiar in that it decomposes explosively on heating and yields a large volume of extremely fine amorphous carbon. Graphite is used in the manufacture of lead pencils, crucibles, polishes, etc.

(c) **Amorphous Carbon**.—This is obtained in the purest state by charring sugar. The resulting mass is boiled with acids to remove the mineral matter and finally heated red-hot in a current of chlorine for quite a while to remove all the hydrogen. It can also be prepared from soot. Amorphous carbon is opaque, black and infusible. At the highest temperature that MOISSAN could reach with his furnace by employing a current of 2000 ampères and 80 volts (obtained with a 300 horse-power engine) it was barely possible to make carbon sublime. The sublimate was graphite. Amorphous carbon has a specific gravity of 1.5–2.3.

Various sorts of amorphous carbon are known. They are probably different allotropic modifications, or mixtures of such. *Gas carbon* and *coke* are obtained as residues in the dry distillation of coal. They conduct heat and electricity. *Wood charcoal* is very porous and can condense large quantities of gases in its pores, e.g. 90 times its own volume of ammonia. When warmed or when the pressure is reduced, these gases all escape again. *Bone-black* is obtained by heating bones away from air; the resulting black mass is treated with hydrochloric acid to remove the phosphates and carbonates present. It has the power of absorbing coloring-matter and certain salts, e.g. lead salts, from liquids. The charcoal obtained from the dry distillation of sugar is noted for its peculiar lustre. These different sorts of charcoal do not consist of pure carbon but contain other substances in small proportions. It is a general rule that carbon conducts heat and electricity better the longer it has been exposed to a high temperature.

177. The various kinds of carbon all find their respective uses. *Soot*,

or *lamp-black*, serves for the preparation of India ink and black paint. *Gas carbon (coke)*, being a good conductor of electricity, is used in the electrical industry. *Wood charcoal* is used in the manufacture of gunpowder; *animal charcoal*, or *bone-black*, as a water-filter to remove coloring matter, ill-smelling gases or injurious salts (lead salts) from drinking-water; it is also employed in enormous quantities in sugar-refineries to decolorize sugar liquids.

By far the most important use of carbon is as a fuel. The heat generated by the burning of coal warms our houses, drives our steam-engines, etc.

The principal kinds used as fuels are *charcoal*, *coke*, *anthracite coal*, *bituminous coal*, *brown coal (lignite)* and *peat*.

*Charcoal* (wood charcoal) is made on a large scale by the colliers. Long sticks of wood are piled in a large heap, covered with sod and ignited at the bottom. The wood smolders away slowly and becomes completely charred. This "charcoal-pit" process is not at all economical, inasmuch as all the volatile products are lost; nevertheless it is carried on extensively (Fig. 52).

*Coke* is the residue in the retorts of the gas-factories after the coal has been deprived of its volatile products by heating.

*Peat* and the *various coals* owe their origin to the same geological process, the slow decay of plant-remains in the absence of air. Peat is the youngest formation and anthracite coal the oldest. During this transition carbon dioxide and methane,  $\text{CH}_4$ , are given off and the remainder becomes richer in carbon and poorer in hydrogen and oxygen than the corresponding chief constituent of plant-tissues, cellulose. The following table shows this:

	Carbon.	Hydrogen.	Oxygen.
Cellulose.....	50.0%	6.0%	44.0%
Peat.....	60.0	5.9	34.1
Brown coal.....	67.0	5.8	27.2
Cannel coal.....	85.8	5.8	8.3
Anthracite coal.....	94.0	3.4	2.6

The plants of which these formations originally consisted are different. Peat appears from its structure to have come chiefly from swampy growths, mosses and the like; mineral coal from extinct plants, gigantic horse-tails (*equiseta*), *lepidodendra* and *sigillariæ*.

**Molecular and Atomic Weight of Carbon.—Chemical Properties.**

178. The carbon molecule contains a large number of atoms. How large this number is it has not yet been possible to ascertain. It is supposed that graphite has a larger number of atoms to the molecule than amorphous carbon and diamond more than graphite, since graphite and diamond are less easily attacked by chemical reagents and because they are denser.

A determination of the vapor density of carbon is of course out of the question. The measurement of the melting-point depression that carbon produces in iron is also impracticable, since we have

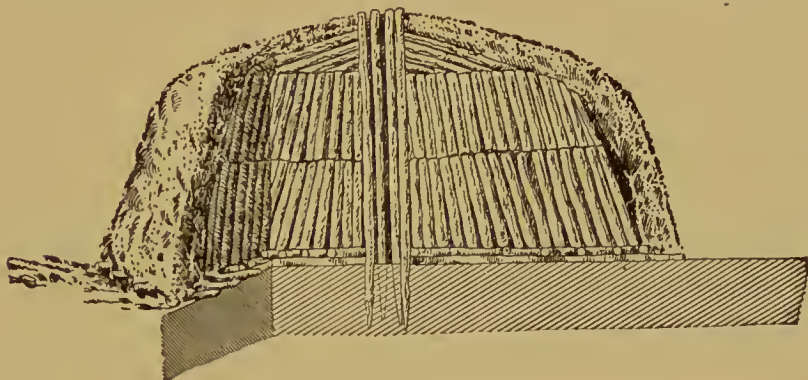


FIG. 52.—CHARCOAL PIT.

no means of measuring temperature differences of  $\frac{1}{50} - \frac{1}{100}^{\circ}$  at the melting-point of iron. Besides, the result would be complicated by the fact that iron forms compounds with carbon.

It can be shown in the following way, however, that the number of atoms in the carbon molecule must be very great. By the oxidation of amorphous carbon with potassium permanganate *mellitic acid* is formed, which contains 12 carbon atoms to the molecule. This makes it quite probable that the carbon molecule contains at least 12 atoms, for in the oxidation of organic substances the products almost always contain either a smaller or the same number of carbon atoms to the molecule. For the following reason it is, however, to be supposed that the number of atoms in the carbon molecule is much greater than 12. When *marsh gas*,  $\text{CH}_4$ , is passed through a red-hot tube, *ethylene*,  $\text{C}_2\text{H}_4$ , is formed among other things. If this is then treated in the same way, *acetylene*,  $\text{C}_2\text{H}_2$ , is obtained, and from this again *benzene*,  $\text{C}_6\text{H}_6$ . On

conducting benzene vapor through a glowing tube, *naphthalene*,  $C_{10}H_8$ , *pyrene*,  $C_{16}H_{10}$ , etc., are formed. If either of the latter is heated still higher (in the absence of air) carbon is deposited. We thus see that as the temperature rises the number of carbon atoms in the molecule steadily increases. The final product of these operations, carbon, will therefore probably contain a considerably larger number of atoms in its molecule than naphthalene or pyrene.

Carbon can unite directly with many elements. At ordinary temperatures it combines with fluorine only. MOISSAN introduced lamp black into fluorine gas, and the carbon commenced to glow; when fluorine was present in excess *carbon tetrafluoride*,  $CF_4$ , was formed. So far no conditions have been found under which carbon will unite with the other halogens directly.

Hydrogen combines with carbon directly to form acetylene and marsh gas, when an electric arc is passed between two carbons in an atmosphere of hydrogen. Of all the many compounds consisting of only carbon and hydrogen these are the only ones which can be obtained by direct synthesis.

Oxygen unites with carbon at an elevated temperature to form carbon monoxide,  $CO$ , or carbon dioxide,  $CO_2$ , according as carbon or oxygen is in excess. If sulphur vapor is passed over red-hot coals, carbon bisulphide,  $CS_2$ , is produced.

The elements of the nitrogen group, N, P, As, Sb and Bi, do not combine with carbon directly. Silicon and carbon unite at the temperature of the electric furnace to form  $CSi$ , *carborundum*, which is so hard that it can be used as a powder for polishing glass and precious stones.

MOISSAN has also found that many metals are able to combine with carbon at a very high temperature, forming *carbides*. This was formerly known to be true of iron and certain other metals.

The difference in the behavior of these carbides towards water is interesting. Iron carbide is unaffected by it; calcium carbide gives acetylene,  $C_2H_2$ ; aluminium carbide yields methane instead; other carbides give mixtures of the two hydrocarbons; uranium carbide produces methane and also liquid and solid hydrocarbons.

179. The *atomic weight of carbon* has been determined with great accuracy by DUMAS and STAS. Carefully dried oxygen was passed through a porcelain tube containing a platinum boat, which

held some graphite or diamond and which had previously been weighed with its contents. The tube was heated red hot and the carbon dioxide resulting from the combustion of the carbon was absorbed in potassium hydrate. By weighing the boat with its contents after the experiment the amount of carbon burned could be determined; by weighing the absorption apparatus before and after, the amount of carbon dioxide was readily found. The averages for the different series of experiments, each of which showed little variation, were as follows:

Ratio by weight of carbon to oxygen in carbon dioxide from the combustion of:

Natural graphite.....	2.9994 : 8.0000
Artificial " .....	2.9995 : 8.0000
Diamond.....	3.0002 : 8.0000.

The ratio of carbon to oxygen in carbon dioxide is thus very close to 3 : 8. As the specific gravity of carbon dioxide points to a molecular weight of 44 for this gas, it must contain, according to this ratio, 12.00 parts by weight of carbon and 32 parts of oxygen. The formula is therefore  $C_xO_2$ . Inasmuch as no carbon compound is known whose molecular weight includes less than 12 parts of carbon, we have  $CO_2$  as the formula; hence the atomic weight of carbon must be **12.00** for  $O = 16$ .

### Compounds with Hydrogen.

**180.** Carbon and hydrogen form a very large number of compounds (*hydrocarbons*), which are more fully discussed in organic chemistry. A very small number will be treated here briefly.

**Methane**, also called *marsh gas* and *fire-damp*, is the only hydrocarbon with just one atom of carbon. It occurs in nature in volcanic gases; moreover, it gushes out of the ground in the neighborhood of the oil-wells at Baku and various places in America. It is an important constituent of "natural gas." It owes the name "marsh gas" to the fact that it arises from swamps, especially when the decaying vegetation at the bottom is stirred up. It is called "fire-damp" because it occurs in coal-beds (p. 234), from which it escapes when they are broken up. It forms a violently explosive mixture with air, which is frequently the cause of mine explosions. Methane results from the dry distillation of many organic substances; hence its occurrence in illuminat-

ing gas in a considerable amount (30–40%). A direct synthesis of it has already been mentioned (§ 178). Ordinarily it is prepared by heating sodium acetate with soda-lime:



BERTHELOT obtained it by conducting a mixture of hydrogen sulphide and carbon bisulphide over red-hot copper:



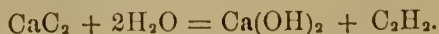
Since both carbon bisulphide and hydrogen sulphide can be obtained by synthesis from their elements, this reaction can be considered as a synthesis of methane.

*Physical Properties.*—Methane is a gas without color or odor. Its specific gravity, 7.98 (H = 1), corresponds to the formula CH<sub>4</sub>. When liquefied it boils at –155° under ordinary pressure. It freezes at –185°. Water dissolves it but little (0.06 vol. at 6°).

*Chemical Properties.*—Methane burns with a faintly luminous flame. It requires a high temperature to break it up. The sparks of a powerful induction-coil or the electric arc are able to dissociate it into its components, acetylene, C<sub>2</sub>H<sub>2</sub>, being also formed, however. If mixed with chlorine the hydrogen is gradually replaced by chlorine and we obtain accordingly CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub>. A mixture of 1 vol. CH<sub>4</sub> and 2 vols. Cl<sub>2</sub> explodes when exposed to the light, forming 4HCl and depositing carbon. Methane has neither basic nor acidic properties.

**Ethylene**, C<sub>2</sub>H<sub>4</sub>, is obtained by heating alcohol with sulphuric acid. It is a gas condensable to a liquid which boils at –103° and congeals at –160°. It has a rather sweet odor and burns with a luminous flame. When conducted into bromine, it quickly forms C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>. It is slightly soluble in water and alcohol. It is contained in illuminating gas.

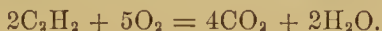
**Acetylene**, C<sub>2</sub>H<sub>2</sub>, is a colorless gas of a disagreeable odor. It is soluble in an equal volume of water at 18° and becomes liquid at 18° under 83 atmospheres. Its hydrogen atoms are replaceable by metals. It is manufactured by decomposing calcium carbide with water:



Calcium carbide is prepared by heating coke with unslaked lime (CaO) in the electric furnace. The calcium formed by the action of carbon on lime unites with carbon at the high temperature of the furnace to form



$\text{CaC}_2$ . Acetylene burns with a vivid flame on coming out of a small orifice under pressure. Efforts are being made to use it for illuminating purposes, since it can be prepared from calcium carbide pretty cheaply, nevertheless it is still difficult to say whether the dangers involved in its use can be completely surmounted by its promoters. When mixed with air and ignited it explodes vehemently; the compounds with metals are also explosive. It is endothermic and can be exploded by fulminating mercury. The combustion of acetylene is another illustration of the rule of §137, that reactions are in most cases of a simpler nature than the chemical equations indicate. The equation here is :



According to this equation the combustion should be heptomolecular. BONE and CAIN proved, however, that the reaction has different stages, the first of which is represented by the bimolecular equation :



$\text{CO}$  and  $\text{H}_2$  then burn further to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

From a kinetic standpoint, it is quite conceivable that polymolecular reactions should be rare, for the probability of a large number of molecules coming together in just such a way that a reaction can take place is indeed very slight. The reaction is more likely to proceed in a way which involves the interaction of only very few molecules.

### Compounds with the Halogens.

181. Of these we shall mention only carbon tetrachloride,  $\text{CCl}_4$ , which is obtained among other ways by the continued action of chlorine on methane. It is a stable compound, a liquid with an odor like chloroform. Boiling-point  $76^\circ$ . Sp. g. = 1.593 at  $20^\circ$ .

At ordinary temperatures it is not attacked by water; however, when the two are heated together at  $250^\circ$  in a sealed tube, carbon dioxide and hydrochloric acid are formed.

### Compounds with Oxygen.

Two oxygen compounds of carbon are known: *carbon monoxide*,  $\text{CO}$ , and *carbon dioxide*,  $\text{CO}_2$ .

#### CARBON MONOXIDE, CO.

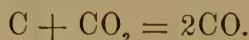
182. This compound is always formed when carbon burns in a limited supply of air or oxygen. A number of carbon compounds

also yield carbon monoxide when burned under the same condition. This gas can also be obtained by the action of carbon on oxygen compounds, e.g. by heating zinc oxide,  $\text{ZnO}$ , with carbon. On passing steam over red-hot coals a mixture of hydrogen and carbon monoxide is produced:

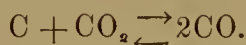


This mixture goes by the name of *water-gas*. It is used on a large scale for heating and lighting, especially in America. For the latter purpose it is charged with the vapor of hydrocarbons rich in carbon, since its own flame is not luminous. The use of the incandescent gas-light (§ 291) makes this "carburetted" unnecessary.

Carbon monoxide is also formed by the reduction of carbon dioxide with red-hot coal:



This reaction is limited by the reverse one; we thus have here an equilibrium expressed by



In order to reduce this to a mathematical form, we must note that coal is a solid; experience has proven that when a solid substance occurs in a chemical system its concentration is constant. We can understand this by supposing that the reaction takes place only in the gaseous state, in this case between carbon dioxide and carbon, the vapor-tension of the latter being extremely low but existing nevertheless. So long as solid coal is present, the gases must be saturated with its vapor, so that at a constant temperature there is a constant pressure, i.e. a constant concentration. If then we call the concentrations of the gases  $p_{\text{C}}$ , etc., the equation becomes:

$$p_{\text{C}} \cdot p_{\text{CO}_2} = k \cdot p_{\text{CO}}^2,$$

$k$  being a constant (at a constant temperature). As, however,  $p_{\text{C}}$  is constant, we can combine it with  $k$ , and so we have

$$p_{\text{CO}_2} = K p_{\text{CO}}^2, \text{ or } K = \frac{p_{\text{CO}_2}}{p_{\text{CO}}^2}.$$

According to LE CHATELIER'S rule (and § 51) the equilibrium

depends here on the pressure; on increasing this, the gas volume is diminished, hence more carbon dioxide must be formed.

Experience has further taught that the proportion of carbon monoxide increases rapidly with rising temperature; at 1050° there is only very little carbon dioxide present. K thus decreases in the above equation as the temperature rises.

The reduction of salts of carbonic acid also furnishes a method of preparing carbon monoxide. If chalk (CaCO<sub>3</sub>) or magnesite (MgCO<sub>3</sub>) is heated with zinc dust, pure carbon monoxide is formed:



*Physical Properties.*—Carbon monoxide is a colorless, odorless gas of a specific gravity of 0.967 (air = 1). It is hard to condense, its critical temperature being —139.5° and its critical pressure 35.5 atmospheres. It boils at —190° and solidifies at —211°. It is only slightly soluble in water.

**183.** *Chemical Properties.*—Carbon monoxide burns with a characteristic blue flame to carbon dioxide.

It is a remarkable fact that this combustion occurs with ease only when the gas is moist; if it and the oxygen also are carefully dried, the action is extremely backward. A carbon monoxide flame goes out, for instance, when it is introduced into a flask of oxygen whose walls are sprinkled with concentrated sulphuric acid (§ 38).

Carbon monoxide can unite with chlorine directly to form *phosgene*, COCl<sub>2</sub>, and also with sulphur (at an elevated temperature) to form *carbon oxysulphide*, COS; both compounds are gaseous. Again it unites directly with nickel and iron, giving the compounds Ni(CO)<sub>4</sub> and Fe(CO)<sub>5</sub> (§§ 214 and 311).

On account of its tendency to combine with oxygen, it displays strong reducing power, especially at high temperatures. Thus metal oxides, like Fe<sub>2</sub>O<sub>3</sub>, CuO, etc., are easily converted into the metals when hot. Some compounds are reduced by carbon monoxide even at ordinary temperatures. Palladium is precipitated from an aqueous solution of palladious chloride and an ammoniacal silver solution (prepared by dissolving silver oxide in ammonium hydrate to the point of saturation) is turned black by the gas

because of formation of the metal. Both of these reactions serve for the detection of carbon monoxide.

An ammoniacal cuprous chloride solution absorbs the gas because of the formation of a compound,  $\text{Cu}_2\text{Cl}_2 \cdot \text{CO} + 2\text{H}_2\text{O}$ , which can be isolated in the crystalline state but decomposes again very readily.

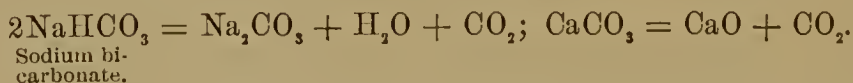
Carbon monoxide is very poisonous, for it unites with the hæmoglobin of the blood, forming *carbonyl-hæmoglobin*, and thereby prevents it from combining with oxygen to form *oxyhæmoglobin*.

The *composition* of carbon monoxide can be determined by exploding a mixture of the gas with oxygen. It is then found that 2 vols. CO unite with 1 vol.  $\text{O}_2$  to form 2 vols.  $\text{CO}_2$ . This together with the vapor density establishes the formula as CO.

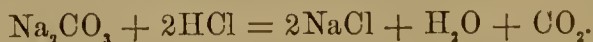
#### CARBON DIOXIDE, CARBONIC ACID ANHYDRIDE, $\text{CO}_2$ .

184. This compound occurs not only by itself but also in combination. It is a regular constituent of the air (§ 106); many mineral waters contain the free gas; in some places of the earth (in the Dog's Grotto at Naples and the famous Poison Valley in Java) it comes up out of the ground and it is also found in volcanic exhalations. The most minerals and rocks contain numerous extremely small cavities, partly filled with liquid carbon dioxide. Combined, it occurs in large quantity in the carbonates of lime and magnesia (§ 176).

Carbon dioxide results from the combustion of carbon in an excess of oxygen and also from the direct decomposition of many salts of carbonic acid (*carbonates*) by heat:



Moreover, it is formed when a carbonate is decomposed by an acid:



By the action of oxygen at high temperatures all carbon compounds are burned with the formation of carbon dioxide. It is also produced by the action of carbon on oxygen compounds, e.g. by heating powdered charcoal with an excess of copper oxide; finally also by the interaction of carbon compounds and oxygen

compounds. This latter action is the basis of the general method for determining the proportion of carbon in organic substances; they are heated together with copper oxide and the carbon dioxide formed is absorbed in a weighed amount of caustic potash.

*Physical Properties.*—Carbon dioxide at ordinary temperatures and pressures is a gas with a somewhat pungent odor and taste. Sp. g. = 1.529 (air = 1). It is thus about half again as heavy as air, so that in those places where it comes out of the earth, as in the Dog's Grotto at Naples, it stays in a layer close to the ground and a dog, for instance, is suffocated while a man can breathe with comfort. Carbon dioxide is easily condensed, becoming liquid at 0° under 35 atmospheres pressure. Its critical temperature is 31.35° and its critical pressure 72.9 atm. Liquid carbon dioxide ("liquid carbonic acid") is manufactured in great quantities and brought on to the market in steel bottles (bombs). It is a very mobile liquid, which is not miscible with water in all proportions. If the liquid is allowed to escape from the bomb into a coarse linen bag (by inverting the bomb and opening the valve), part of it vaporizes, absorbing thereby so much heat that the remainder solidifies in white flakes. A mixture of this solid carbon dioxide with ether, alcohol or acetone is often used as a freezing mixture; it enables us to obtain a temperature of - 80°, and even - 140° *in vacuo*. When liquid carbon dioxide is cooled down in a sealed tube, it congeals to an icy mass, which melts at - 65°.

At 15° carbonic acid gas dissolves in its own volume of water (more accurately 1.0020 vol.); at 0° in 1.7967 vol. In alcohol it is still more soluble.

*Chemical Properties.*—Carbon dioxide is a very stable compound; it is only decomposed by intense heat (1300°) or by the continued action of induction sparks, breaking up into oxygen and carbon monoxide. This decomposition never completes itself, for just so soon as a certain amount of these gases have been formed, they reunite with explosion. At the moment before the explosion the amount of carbon dioxide still present becomes no longer sufficient to dilute the mixture of oxygen and monoxide enough to hinder an explosion; the *explosive limit* is reached.

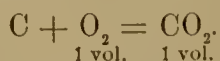
Carbon dioxide cannot be farther oxidized; it is therefore not combustible. In general it cannot support combustion either. There are, however, certain substances that take up oxygen from

it when hot; if carbon dioxide is mixed with hydrogen and passed through a red-hot tube, carbon monoxide and water are formed; when led over glowing carbon or when heated with phosphorus it is reduced to carbon monoxide. If a burning magnesium ribbon is lowered into carbon dioxide, the oxide of the metal is formed, carbon being deposited also; the same thing happens when sodium or potassium is heated in dry carbon dioxide.

The aqueous solution of carbon dioxide reacts a trifle acid; it is supposed that it contains a compound  $\text{H}_2\text{CO}_3$ , of which many salts are known. This acid, *carbonic acid*, has not yet been isolated in the free state, however, since it gives off gaseous carbon dioxide ("carbonic acid gas") when the solution is boiled or frozen. If its salts (carbonates) are treated with an acid, no  $\text{H}_2\text{CO}_3$  is obtained either, for it breaks up forthwith into water and carbon dioxide. Carbonic acid is a very weak acid; it is liberated from its salts by almost every other acid. By adding hydrochloric acid to a carbonate  $\text{H}^+$ -ions are introduced into the liquid and they unite with the  $\text{CO}_3^{--}$ -ions to form integral molecules of  $\text{H}_2\text{CO}_3$ . These, however, break up largely into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , the latter of which can only remain in solution up to a certain amount at a constant pressure, so that all in excess of this passes out. As a result the concentration of the  $\text{H}_2\text{CO}_3$  molecules cannot exceed a definite and, in this case, low limit. Since moreover the ionization of these molecules is very weak, in reality all of the carbonate is decomposed by the strong acid (§ 73).

The neutral carbonates of the alkalies are soluble in water, those of the other metals insoluble; the acid carbonates are, however, mostly soluble in water. Calcium carbonate, e.g., dissolves in water containing carbonic acid. The solutions of such acid carbonates give off carbon dioxide on simply boiling, however, and the neutral carbonates are precipitated. In the solid state also the acid carbonates give off carbonic acid gas very readily on warming.

*Composition of Carbon Dioxide.*—In connection with what was stated in § 179 it is an important fact that no change of volume occurs when carbon burns in an excess of oxygen:



A still higher oxygen compound of carbon is known, although only in the form of a salt, **potassium percarbonate**,  $\text{K}_2\text{C}_2\text{O}_6$ . It is produced by the

electrolysis of a saturated potash solution at  $-15^{\circ}$ ; this synthesis may be considered as analogous to that of persulphuric acid (§ 91). Here the potash is split up in  $K$  and  $KCO_3$ ; the latter ions are discharged at the anode and two of them unite to form  $K_2C_2O_6$ . It separates out as a sky-blue precipitate, which after being dried in a phosphorus pentoxide desiccator is a light-blue powder consisting of  $K_2CO_3$  and  $K_2C_2O_6$ . Even gentle warming decomposes the percarbonate :

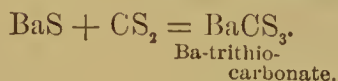


It acts therefore as a strong oxidizing agent ; it oxidizes lead sulphide to the sulphate, bleaches indigo, etc. Manganese dioxide and lead peroxide are converted into the respective carbonates in a vigorous reaction, in which case it acts as a reducing agent.

### Other Carbon Compounds.

**185. Carbon bisulphide,  $CS_2$ ,** is prepared by direct synthesis, by passing sulphur vapor over red-hot charcoal. It is a highly refractive, almost colorless liquid, having an ethereal odor when pure. It boils at  $46^{\circ}$ , is insoluble in water and has a specific gravity of 1.262 at  $20^{\circ}$ . Carbon bisulphide is poisonous and extremely inflammable, hence a very dangerous liquid to handle. It is an invaluable solvent for fats and oils and is therefore used on a large scale for the extraction of these substances. It is also used in vulcanizing rubber. Carbon bisulphide is endothermic ; it can be made to explode by fulminating mercury ; nevertheless under ordinary conditions it is quite stable.

Carbon bisulphide is a sulpho-anhydride (§ 164). With alkali sulphides it forms sulphosalts, *trithiocarbonates* :



The barium salt is yellow and difficultly soluble in cold water. The *trithiocarbonic acid*,  $H_2CS_3$  can be obtained from its salts with dilute acids as an unstable oil. The *potassium salt* is used for exterminating grape-lice.

**Cyanogen,  $(CN)_2$ ,** can be prepared by heating mercuric cyanide,  $Hg(CN)_2$ , or by treating a solution of potassium cyanide with copper sulphate solution. It is possible that first cupric cyanide is formed and that this at once breaks up into cuprous cyanide and cyanogen :



Cyanogen has a penetrating odor. When liquefied it boils at  $-20.7^{\circ}$ . It is unaffected by high temperatures. It dissolves in water, but the solution deposits amorphous brown flakes after a while. It burns with a purple-tinged flame according to the equation:



the reaction, however, is not trimolecular, the first stage being



i.e. a bimolecular process (see § 180). Chemically it resembles the halogens. Potassium burns in cyanogen as in chlorine, forming *potassium cyanide*, KCN. If cyanogen is passed into potassium hydrate solution, the same cyanide is formed together with *potassium cyanate*, KCNO, analogous to the formation of the chloride and hypochlorite, KCl and KClO, on leading chlorine into potassium hydrate (§ 56). *Silver cyanide* is curdy, insoluble in water and dilute acids and soluble in ammonia, like silver chloride.

**Hydrogen cyanide**, HCN (*prussic acid*) is important in inorganic chemistry because of the numerous complex salts which it forms. Many of them, particularly those containing alkalies, are soluble in water and crystallize beautifully. Salts of prussic acid are formed in general when carbon, nitrogen and a strong base come in contact at red heat, e.g. when a mixture of carbon and potassium carbonate are heated red-hot in a current of nitrogen. On heating nitrogenous organic substances with an alkali, cyanides are also formed. Ammonium cyanide is produced by passing ammonia over red-hot charcoal. If induction sparks are sent through a mixture of acetylene and nitrogen, hydrogen cyanide is formed. Ordinarily hydrocyanic acid is prepared by distilling yellow prussiate of potash (§ 308) with dilute sulphuric acid; the distillate is an aqueous solution, which yields anhydrous prussic acid by fractional distillation, the last traces of water being removed by phosphorus pentoxide. *Anhydrous hydrogen cyanide* is a colorless liquid with an odor like bitter almonds. It boils at  $26^{\circ}$ ; its melting-point is  $14^{\circ}$ . The pure acid is stable but dissolved in water it decomposes with the deposition of insoluble amorphous brown substances. Like most cyanides it is a very dangerous poison. As



an antidote very dilute chlorine gas may be inhaled, or hydrogen peroxide taken.

The electrical conductivity of an aqueous prussic acid solution is very low; it is therefore one of the weakest acids.

As to its salts, those of the alkalies and alkaline earths, and also mercuric cyanide, are soluble in water, the others insoluble.

### The Flame.

186. A flame is produced by the burning of a gas; solids, like iron, carbon, etc., burn without a flame. If a flame is observed during the burning of mineral coal, a candle or the like, it is due

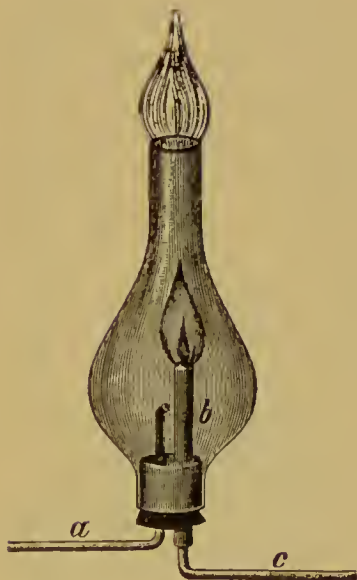


FIG. 53.—REVERSE FLAME.

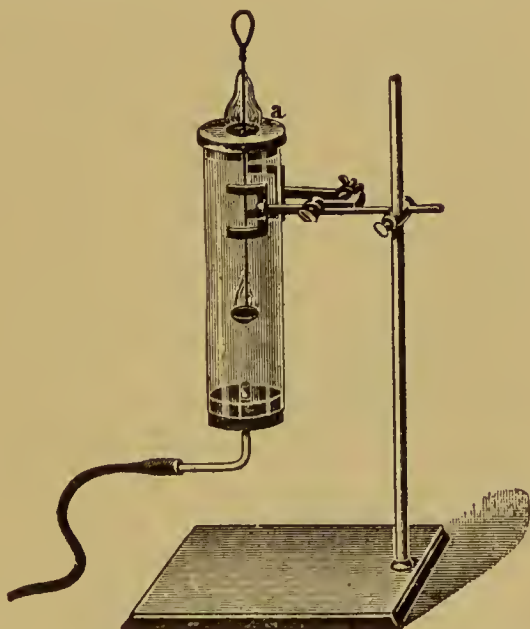


FIG. 54.—POTASSIUM CHLORATE FLAME.

to the fact that at that high temperature gaseous decomposition-products are formed, which burn. If a gas burns in the air, it is called a combustible gas and the oxygen of the air is called the supporter of the combustion. These expressions in common use are only relative terms; it is possible to light the oxygen and have it burn with a flame in a gas which is ordinarily called combustible. This phenomenon is illustrated in a way by the *reverse flame*.

This can be easily obtained with the aid of the apparatus of Fig. 53. A lamp-chimney is fitted with a two-hole cork at its lower end. Through

the narrower hole of the cork a small tube *a* is inserted for conducting in the gas, through the wider hole a tube *b* for the admission of air. The chimney is first removed and the gas coming out of tube *a* lighted and so regulated as to produce a small flame. Then the chimney is replaced; the flame continues to burn quietly, inasmuch as plenty of air is supplied by the wider tube. Thereupon the gas-supply is gradually increased and at a certain moment the small flame at the end of *a* is extinguished and a large pale flame appears at the end of *b*; it is air burning in the gas which fills the chimney. This is the reverse flame of air in illuminating gas. At the same time the excess of gas escaping at the top ignites in the outside air, so that the apparatus presents both a direct and a reverse flame at the same time. That it is really air that burns at the mouth of *b* is proven by introducing a tiny gas-flame by means of the tube *c* into the flame of the wide tube *b*; the small flame continues to burn.

Substances that give up oxygen are capable of burning when surrounded by a combustible gas. The experiment can be carried out with potassium chlorate as follows: Illuminating gas is conducted into a glass cylinder (Fig. 54) and lighted at the top, where the cylinder is covered by a thin piece of metal with a hole in it. A little potassium chlorate is then lowered into the flame by means of a deflagrating spoon and heated till oxygen comes off freely. If the bowl is then dipped down in the cylinder, the oxygen burns with a very luminous flame, which is colored violet-blue by the vaporization of some potassium salt.

We saw above (§ 27) that a hydrogen flame continues to burn in chlorine with the formation of hydrochloric acid; on the other hand chlorine can also be made to burn in hydrogen. For this purpose a cylinder closed at the top is filled with hydrogen and lit at the lower edge. A tube through which chlorine is supplied is then brought in contact with this flame and inserted in the cylinder. The chlorine burns on.

187. A flame may be luminous or non-luminous. It gives light when solid particles are suspended in it. An ordinary gas-flame is luminous because particles of carbon, set free by the combustion, are made to glow. On introducing a cold object into the flame they are deposited as soot. The light of the WELSBACH *incandescent gas-light* is produced by the glowing incombustible mantle (§ 291).

Such flames give a continuous spectrum (§ 263). Many gases, which yield only gaseous products on burning, give either a very faint light or none at all, e.g., hydrogen, carbon monoxide, etc. However, when hydrogen burns in oxygen of 20 atmospheres pressure, its flame is strongly luminous. Other incandescent gases, such as the vapors of certain metals, can render a flame luminous

even at ordinary pressure, imparting to it a definite color. Colored flames of this sort give a line spectrum (§ 263).

A gas flame, whose light is due to incandescent particles of carbon, is made non-luminous by mixing the gas with air before the combustion. This is the principle of the BUNSEN burner (Fig. 55), which is used in all laboratories and quite extensively also, with some variation or other, in heating and cooking apparatuses (gas stoves).

The Bunsen burner consists of a base in which is a tube for supplying the gas, which escapes from a narrow orifice at *a*. Here it mixes with air that enters through the lateral holes in *b*. This mixture burns with a colorless flame when ignited at the top of *c*.

The opinion was originally held that the loss of luminosity of the flame is due to the *oxygen* of the air, the latter causing the complete combustion of the carbon particles. As has since been shown, however, the dilution of

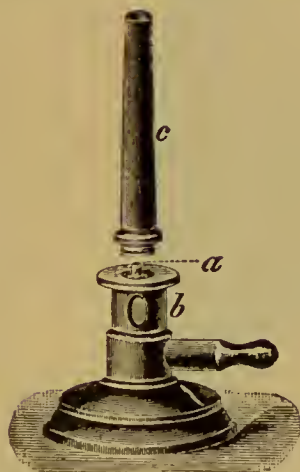


FIG. 55.—BUNSEN BURNER.

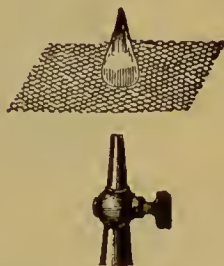


FIG. 56.—EFFECT OF A WIRE GAUZE ON A FLAME.

the burning gas with nitrogen also has a part in it: if illuminating gas is mixed with twice or thrice as much nitrogen, the former burns with a colorless flame.

With the aid of a wire gauze a burning gas mixture can be cooled so low that the combustion cannot propagate itself through the gauze, in other words, the flame does not get through the gauze. If gas is allowed to flow out of a Bunsen burner and a wire gauze is held across the current a short distance from the orifice, the gas can be lit above the gauze without the flame springing back to the burner (Fig. 56).

It was by experiments such as these that DAVY was led to discover his *miner's safety-lamp*. As Fig. 57 shows, this consists of an oil-lamp, the flame of which is surrounded by a wire cage. A combustible gas mixture can catch fire inside of the lantern, but the fire cannot pass through the gauze to the outside.

188. The *temperature of the flame* is much lower than we might suppose. Since, when hydrogen burns in oxygen, 57.2 kg.-calorics are produced by every 18 g. of the mixture, and the specific heat of steam is 0.48, this amount of heat ought to raise the 18 g. steam to a temperature of  $\frac{57.2}{0.018 \cdot 0.48} = 6600^\circ$ . In reality the temperature of the flame does not exceed  $2500^\circ$ . This difference between



FIG. 57.—MINER'S SAFETY-LAMP.

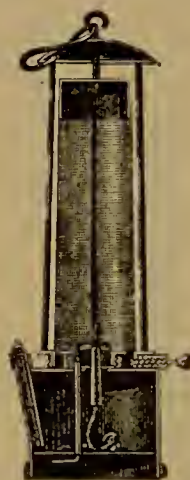


FIG. 58.—SECTION OF THE PRECEDING.

calculation and observation is due to the fact that on account of dissociation only a partial combination of hydrogen and oxygen takes place in any part of the flame. The temperature of  $6600^\circ$  could indeed be obtained at any point, if the gases united there completely and momentarily; but this is impossible, for above  $1300^\circ$  the formation of the compound is checked by the opposite process, the dissociation of steam. Therefore what occurs must be this: oxygen and hydrogen, when brought together at the aperture, combine and effect a certain rise of temperature; in the same measure as the system in equilibrium (hydrogen, oxygen, steam) cools off, new amounts of the gases unite. Their combustion cannot therefore take place at any particular point but must be gradual

throughout the whole extent of the flame and at any one point the temperature cannot exceed a certain limit, which is determined by the degree of dissociation of the combustion product.

189. *Zones of a luminous flame.* Let us take a candle flame, for example. In the central zone (1 in the diagram Fig. 59) there is no combustion. The stearin of the candle is here converted by the heat of the flame into volatile combustible products. In a large candle this can be proven in the manner shown in Fig. 59. The narrow tube conducts off the inflammable gases and they can be lit at the outer end.

The hollowness of a flame can be demonstrated in various ways;

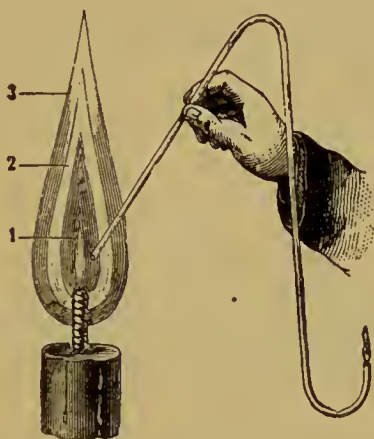


FIG. 59.—ZONES OF A LUMINOUS FLAME.

in a Bunsen burner, for instance, by placing a match-head in the center, where it does not ignite, or by holding a thin platinum wire across a flame; the wire only glows at the edges of the flame.

The dark central zone of the flame is next surrounded by the luminous zone (2). Here the volatilized hydrocarbon is decomposed with the separation of carbon, because the air-supply is insufficient for complete combustion. These carbon particles become incandescent and so make the flame luminous. Finally there is the blue outer zone (3), in which the glowing particles of carbon are burned by direct contact with the air. It radiates very little light.

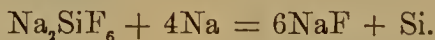
The amount of solid carbon in a flame which is raised to incandescence and hence gives light is very small, as the following calculation shows. The substances in burning illuminating gas which break up with the liberation of carbon are chiefly benzene and ethylene. The former makes up

about 1, the latter about 4, per cent by volume of the gas. If we assume that the benzene is completely broken up and the ethylene only half, then the total amount of carbon deposited by 1 liter of burning illuminating gas is about 54 mg. The volume of the luminous part of a gas-flame with a consumption of 150 liters per hour amounts to about 2 c.c. (reduced to 0°), so that the mass of solid incandescent carbon present in it is only  $\frac{2 \times 54}{1000} = 0.1$  mg.

## SILICON.

**190.** This element in combination with oxygen is one of the principal constituents of the earth's crust (§ 8). In the free state, however, it does not occur in nature, being found almost exclusively as *silica*,  $\text{SiO}_2$ , or in the *silicates*. Sand and the many varieties of quartz are different forms of natural silicon dioxide; the number of silicates is very large.

Free silicon is obtained by heating sodium fluosilicate,  $\text{Na}_2\text{SiF}_6$ , with sodium:



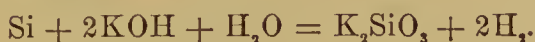
The sodium fluoride can be removed by water. Another method is to heat 40 parts of fine white sand, that must be well dried, with 40 parts of magnesium in a wide test-tube. As soon as the reaction has begun at any point, it spreads of itself throughout the entire mixture.

*Allotropic Forms.*—The silicon thus obtained is a brown amorphous powder; it can be fused under a layer of molten sodium chloride and obtained crystalline on cooling. The latter form is best obtained by heating a mixture of potassium fluosilicate with sodium and zinc. The silicon produced is at once dissolved by the liquid zinc and on cooling separates in crystals, which can be freed from the metal by dissolving the latter in hydrochloric acid. These crystals are regular, black, of a high lustre and a specific gravity of 2.49. They are very hard, and are not at all or only slightly attacked by the reagents which attack amorphous silicon. If silicon is heated in the electric furnace, it vaporizes and condenses again in small globules, mixed with a little gray powder and some silica.

*Chemical Properties.*—Amorphous silicon takes fire when heated in the air, burning to silica. It unites with fluorine at ordinary temperatures, the combustion being marked by a glow; it only

unites with the other halogens at red heat. At an elevated temperature it combines with nitrogen and some metals; these *silicides* have been prepared mainly by MOISSAN in his electric furnace.

It is indifferent towards sulphuric, nitric and hydrochloric acids. Hydrofluoric acid dissolves it, however, with the evolution of hydrogen. Hydrogen chloride gas reacts with it at a high temperature, forming silicon tetrachloride and silico-chloroform. It dissolves in a hot solution of sodium or potassium hydrate, producing hydrogen and a silicate:

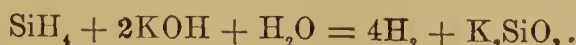


#### Hydrogen Silicide, $\text{SiH}_4$ .

191. This gas is obtained by adding freshly prepared magnesium silicide to hydrochloric acid. The magnesium silicide is prepared by heating sand with an excess of magnesium powder, or better by fusing 40 parts of anhydrous magnesium chloride with a mixture of 35 parts of sodium fluosilicate, 10 of sodium chloride and 20 of sodium. The hydrogen silicide so obtained is mixed with hydrogen. It can be gotten pure from an organic derivative of silicon, tri-ethyl silicoformate, by heating:



Hydrogen silicide, or silicon tetrahydride, is a gas, which becomes liquid at  $-1^\circ$  under a pressure of 100 atmospheres. It has a disagreeable odor. It takes fire in the air; each bubble that escapes from the generator forms a cloudy ring of  $\text{SiO}_2$  aq. If, however, the hydrogen silicide is perfectly pure, it does not ignite spontaneously in the air at ordinary temperatures, but under reduced pressure it does. The self-ignition of impure gas is to be ascribed to the dilution with hydrogen. We have therefore in this case phenomena similar to those in the case of hydrogen phosphide (§ 137). Heat decomposes it readily into Si and  $2\text{H}_2$ . It burns in a chlorine atmosphere. It is decomposed by an alkali solution according to the equation:



### Halogen Compounds of Silicon.

**192. Silicon tetrachloride**,  $\text{SiCl}_4$ , is prepared by mixing fine quartz sand with charcoal and heating in a current of chlorine. An easier method is by heating silicon in a current of chlorine at  $300^\circ$ – $310^\circ$ . Silicon tetrachloride is a liquid with the specific gravity 1.52408 at  $0^\circ$  and the boiling-point  $59.57^\circ$ . It is instantly decomposed by water, forming hydrochloric acid and  $\text{SiO}_2$  aq.

In the preparation of the tetrachloride from silicon (obtained from sand and magnesium) **silicon trichloride**,  $\text{Si}_2\text{Cl}_6$ , is obtained as a side-product. This is also easily decomposed by water, forming an insoluble solid, **silico-oxalic acid**  $(\text{SiO}_2\text{H})_x$ .

**Silico-chloroform**,  $\text{SiCl}_3\text{H}$ , obtained by heating silicon in a current of hydrochloric acid gas (§ 190), is a colorless, strongly smelling compound, which fumes in the air, boils at  $34^\circ$  and is decomposed by water.

**193. Silicon tetrafluoride**,  $\text{SiF}_4$ , can be obtained by warming a mixture of sand and calcium fluoride with concentrated sulphuric acid:



It is a colorless gas with a very pungent and suffocating odor; it condenses under 9 atm. pressure or by cooling to  $-160^\circ$ . When perfectly dry, it does not attack glass.

Silicon fluoride is also formed by the action of hydrogen fluoride on silicates; the silica is first set free from them and then attacked in the way just described. Glass-etching (§ 53) depends on this action.

By the repeated treatment of silicates with hydrous hydrofluoric acid all the silicic acid is driven off as silicon fluoride. The bases which were in combination with the silicic acid are left behind in the form of fluorides. They can be transformed into sulphates by warming with sulphuric acid and then converted into a form suitable for *analysis*. We have here a very useful means of determining the metals present in the silicates.

Water decomposes silicon fluoride as follows:



The compound  $\text{H}_2\text{SiF}_6$  is called **hydrofluosilicic acid**; it is known only in aqueous solution. If the latter is evaporated,  $\text{SiF}_4$  escapes and  $\text{HF}$  stays in solution.



The decomposition of silicon fluoride is usually demonstrated by the following experiment: The compound is generated in the prescribed manner in a flask (Fig. 60), whereupon it is conducted through a doubly-bent glass tube into a cylindrical jar containing a little mercury (into which the tube opens) and on top of this some water. Every bubble of gas that rises from the mercury into the water generates in the latter a cloud of  $\text{SiO}_2$  aq. If the glass tube opened directly in water, it would soon become stopped up with silicic acid.

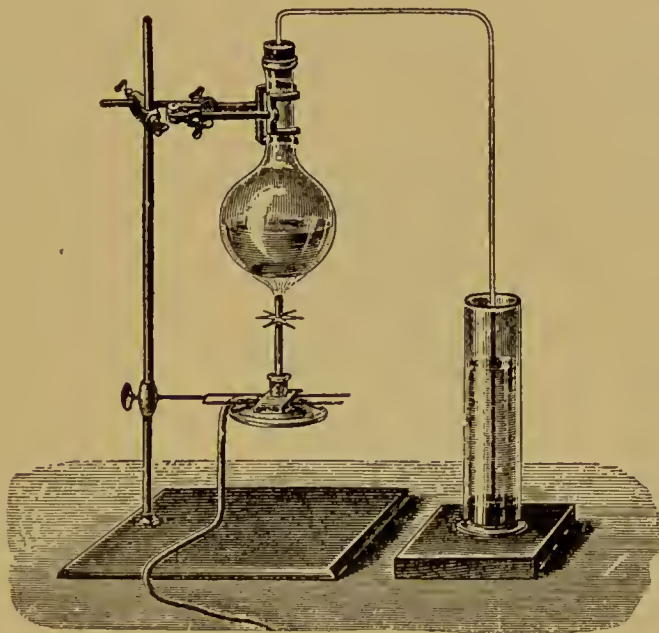


FIG. 60.—PREPARATION OF HYDROFLUOSILICIC ACID.

The solution of hydrofluosilicic acid reacts acid; it dissolves metals with the evolution of hydrogen and behaves in all respects like an acid. A hydrate,  $\text{H}_2\text{SiF}_6 + 2\text{aq}$ , is known in the solid state. It melts at  $19^\circ$ . It is obtained by leading silicon fluoride into concentrated hydrofluoric acid. Most of the salts of hydrofluosilicic acid are soluble in water; the potassium salt is difficultly so, however, and the barium salt is insoluble.

When hydrofluosilicic acid and silicic acid are brought together, on the other hand, silicon fluoride and water are formed. It therefore follows that the decomposition of silicon fluoride by a definite amount of water must have a limit.

Hydrofluosilicic acid is used in hardening objects made of gyp-

sum (this is due probably to the formation of calcium fluoride) and also in analytical chemistry.

### Oxygen Compounds of Silicon.

194. Only one such compound is known: *silicon dioxide*, or *silica*.

#### SILICA, $\text{SiO}_2$ .

This compound occurs in astonishingly large quantities and in a great number of varieties in the solid crust of the earth. It is found crystallized as *rock crystal*, *quartz* (when colored brown, called *smoky quartz*), *amethyst* (the more beautiful sorts being used for ornament), *tridymite*, *onyx*, *cat's-eye*, etc. Sand is largely silica; sandstone also belongs here and so does *jasper* (usually colored red with ferric oxide and having a conchoidal fracture). *Opal* is an amorphous variety, containing varying amounts of water.

Silica can be prepared artificially as an amorphous white powder by heating silicic acid.

*Physical Properties.*—In the crystallized state silica is very hard and insoluble in water and has a specific gravity of 2.6. It is very difficultly fusible; in the oxy-hydrogen flame it softens and can be drawn out into extremely fine threads that are so tenacious and display so regular a torsion that they are frequently used in suspending magnets, etc., in physical instruments. It can be made to boil vigorously in the electric furnace; the vapor condenses in woolly flakes. Quartz that has been fused has a very small dilatation-coefficient; this explains why objects made of it can endure very sudden changes of temperature. A tube of quartz, for instance, can be thoroughly heated and then thrust into cold water at once without cracking.

*Chemical Properties.*—Especially in the crystallized condition silica is very little acted upon by acids except hydrofluoric acid (§ 193). Fused alkalis dissolve it, forming alkali silicates. It can be reduced by carbon in the electric furnace, carborundum (§ 178) being formed. It is also reduced by heating with magnesium (§ 190.)

#### Silicic Acids.

195. When a solution of potassium or sodium silicate (*water-glass*) is treated with hydrochloric acid, a very voluminous, gelat-

inous mass separates out; this consists of hydrous silicic acid corresponding to the general formula  $\text{SiO}_2 \cdot \text{aq}$ . After being washed with water and dried in the air it is a fine white amorphous powder of the approximate composition  $\text{H}_2\text{SiO}_3$ . Freshly precipitated silicic acid is slightly soluble in water, but more so in dilute hydrochloric acid. If, therefore, water-glass is introduced into an excess of hydrochloric acid, the silicic acid stays in solution; it can be separated from the sodium chloride simultaneously formed, by the following process:

The solution is put into a shallow cylinder or a flask with its bottom cut off (Fig. 61), which is closed at the bottom with a piece of

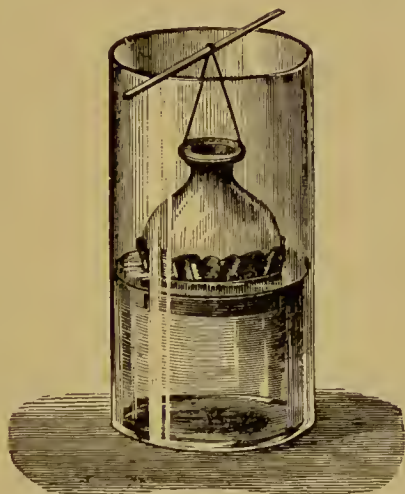


FIG. 61.—DIALYZER.

parchment paper or bladder. This flask hangs in a wider vessel, in which the water can be continuously renewed by means of a siphon. The salt goes through the parchment, but the silicic acid does not. This process is called **dialysis** and the apparatus a *dialyzer*. GRAHAM found that crystallizable substances in solution (*crystalloids*) are able to pass through such membranes, while other substances, which he called *colloids*, are not. In the latter class are glue, gums, gelatine, albumen—in short, many amorphous substances occurring in the animal and vegetable kingdoms. Purification by dialysis is also possible with certain inorganic substances besides silicic acid.

From a pure solution thus prepared—called a *colloidal* solution—the silicic acid is precipitated (coagulated) by the addition of a

small amount of certain salts, e.g. sodium carbonate or hydrochloric acid. This is characteristic of such solutions. They also show still other peculiarities. On evaporation they do not yield crystals but an amorphous, glutinous mass, which is no longer wholly soluble in water. When the boiling-point or freezing-point of a colloidal solution is determined, it is found to be nearly the same as that of the solvent. From this we may conclude either that the molecular weight of the colloidal substance is very great, or that such a solution is not a true one but only a suspension of extremely finely divided particles. Other phenomena confirm the latter view. When, for instance, a liquid which undoubtedly contains such particles, e.g. clay suspended in water or water to which has been added a few drops of milk, is penetrated by a pencil of light rays, the part of the liquid traversed by the rays is luminous, and the diffused light shows itself to be polarized. These very properties are shown by the colloidal liquid obtained by introducing hydrogen sulphide into a solution of arsenious oxide. That this yellow liquid, on the other hand, is a colloidal solution of arsenious sulphide is proved by the fact that this sulphide is precipitated by adding hydrochloric acid or a salt solution.

Silicic acid precipitated from the colloidal solution dries slowly in the air to an amorphous white powder, which still contains a considerable amount of water; the latter is given up slowly in a desiccator over sulphuric acid.

Amorphous gelatinous precipitates like that formed by silicic acid are also known with other compounds. They are called *hydrogels* and have special properties, as VAN BEMMELEN has shown. When freshly precipitated and dried on a porous plate they contain a considerable proportion of water. If they are then placed in a desiccator, they give off their water with constant velocity (i.e. the same amount during equal intervals) and the vapor tension during this process does not vary perceptibly from that of water.

When a certain percentage of water is reached, the vapor tension, and with it the velocity of loss of water, begins to decrease and with such regularity that a curve having the compositions of the hydrogel for abscissæ and its vapor tensions for ordinates shows no breaks.

When such a hydrogel loses its water, it also undergoes a change in molecular structure, for, while it can take up water again in contact with moist air, the vapor tensions corresponding to the same composition before and after the dehydration are greater afterward; in other words, the water is less firmly held in it.

A further peculiarity of the hydrogels is that they absorb alkalis and salts from solution in such a way that the concentration of these substances

is greater in the hydrogel than in the solution. This absorptive power diminishes when the fresh hydrogel is altered by standing under water or by drying.

Since silicon tetrachloride is changed to silicic acid by water, just like phosphorus pentachloride to phosphoric acid (§ 145), we can consider the compound as the basis from which the remaining silicic acids are derived. The latter can in general be represented by the formula  $m\text{Si}(\text{OH})_4 - n\text{H}_2\text{O}$ .

These **polysilicic acids** have indeed not been isolated, but many of their salts and double-salts are known, which occur as minerals in nature. It is a striking fact that, while the great ability of the carbon atom to combine with other carbon atoms is the foundation of the organic world, the quadrivalent element silicon, so closely allied to carbon, is by reason of its ability to form complex silicates the basis of a very extensive part of the inorganic world.

The silicates of potassium and sodium are soluble in water, those of the other metals insoluble, as are also most of the double silicates of the alkalies.

In the soil hydrous silicates are found whose bases are usually lime and alumina. In contact with alkali salts these undergo a double decomposition, an insoluble potassium aluminium silicate, for example, being formed together with chloride of calcium, which is taken off by the underground water. This phenomenon is said to be caused by the *absorptive power* of the soil; it plays an important rôle in the determination of soil-values. It is this that holds back the potash, an invaluable nutrient, which is furnished to the soil in the form of potassium salts and would otherwise be quickly washed off by the rain because of its solubility.

The soluble phosphates are "absorbed" by the soil in the same way. This is mainly to be ascribed to the lime they contain, by which insoluble tri- or dicalcium phosphate is formed; to some extent this absorption may be caused also by basic lime silicates.

#### Silicon Compounds of Other Elements.

**196. Silicon sulphide**,  $\text{SiS}_2$ , is produced when carbon bisulphide vapor is led over a mixture of charcoal and silica at red-heat. It forms long, silken needles, which are broken up by water into  $\text{SiO}_2$  aq and hydrogen sulphide.

**Silicon nitride**,  $\text{Si}_2\text{N}_3$ , a white amorphous substance, results from the heating of silicon in an atmosphere of nitrogen. (For metal silicides *cf.* § 190.)

## GERMANIUM.

197. This element is of extremely rare occurrence. It was discovered by WINKLER in an argentiferous mineral, *argyrodite*,  $\text{GeS}_2 \cdot 3\text{Ag}_2\text{S}$ , found in Freiberg in Saxony. Germanium is obtained from the mineral by heating it with hydrogen or carbon. It forms grayish white octahedrons with a metallic lustre and a specific gravity of 5.469 at  $20^\circ$ . It melts at  $900^\circ$ . At ordinary temperatures it is unaffected by the air; at red-heat it burns, forming white fumes of germanium oxide,  $\text{GeO}_2$ . Like silicon, germanium is insoluble in hydrochloric acid; nitric acid, however, converts it like tin into the hydrate of a dioxide. It is dissolved by molten alkalis. It does not color the flame of a Bunsen burner but it gives a spark-spectrum (§ 263). Two series of compounds of this element are known, which are derived from the oxides  $\text{GeO}$  and  $\text{GeO}_2$ ; the *ous* compounds are easily oxidized to the higher form, germanic acid. No hydrogen compounds are known.

Of the chlorine compounds  $\text{GeCl}_2$  is little studied;  $\text{GeCl}_4$ , **germanic chloride**, can be prepared directly from the elements. Finely powdered germanium takes fire in chlorine.  $\text{GeCl}_4$  is a very mobile liquid, which fumes in the air and boils at  $87^\circ$ . It is broken up by water, forming  $\text{Ge}(\text{OH})_4$ .

**Germanium tetrafluoride.**  $\text{GeF}_4$ , a gas, behaves just like  $\text{SiF}_4$  in the presence of water; the **hydrofluogermanic acid** is formed, whose potassium salt is likewise rather insoluble.

## Oxygen Compounds of Germanium.

**Germanious oxide**,  $\text{GeO}$ , is produced by heating the corresponding hydroxide; it is a steel-gray powder.  $\text{Ge}(\text{OH})_2$  forms when potassium hydrate is added to the solution of the dichloride.

**Germanium dioxide**,  $\text{GeO}_2$ , is also produced by heating the corresponding hydroxide, or by roasting the element or its sulphide or by treating it with nitric acid. It is a white powder of a specific gravity of 4.703 at  $18^\circ$  and unaffected by heat. It is slightly soluble in water (1 part in 95 parts of water at  $100^\circ$ ) and imparts to it an acid reaction. The **hydroxide** has an entirely acid character, since it only forms salts with bases. It dissolves in carbonates when fused; it is insoluble in acids.

## Sulphur Compounds of Germanium.

**Germanious sulphide**,  $\text{GeS}$ , is produced by heating the sulphide in a current of hydrogen and can therefore be obtained directly from argyrodite. It sublimes in thin plates that are grayish black and of a metallic lustre in reflected light and yellowish red in transmitted light.

**Germanium disulphide**,  $\text{GeS}_2$ , separates as a white precipitate, when hydrogen sulphide is passed into the solution of germanium dioxide in

strong hydrochloric acid. In moist air it decomposes, giving off hydrogen sulphide. It dissolves in alkalies and alkali sulphides to form sulpho-salts.

For germanium *cf.* also § 218.

### TIN.

198. This metal is not very widely distributed on the earth; in some places, however, it is found in quite large quantities. The principal tin-mines of Europe are those in Cornwall; even the Phœnicians obtained tin there. The most important present localities are on the group of islands lying east of Sumatra (Banca, Billiton, Sinkop, etc.) There the metal occurs in the form of tin-stone (*cassiterite*,  $\text{SnO}_2$ ); it is found in quadratic crystals, which are usually colored brown or black by a small amount of iron. In order to extract the metal, the ore is at first roasted, to eliminate any sulphur or arsenic it may contain, and then reduced with carbon. The tin thus obtained is refined by liquation, i. e. by fusing again at a low temperature and pouring it off from the less fusible alloy of tin with iron and arsenic. It is then melted once more and stirred with a wooden pole (branch of a tree), whereby the oxide still remaining is reduced. The Banca tin is nearly chemically pure.

*Physical Properties.*—Tin is a silvery-white metal, melting at  $232.7^\circ$  and volatilizing between  $1450^\circ$  and  $1600^\circ$ . Sp. g. = 7.293 at  $13^\circ$ . It has a crystalline structure which can be made visible by moistening with hydrochloric acid, whereupon peculiar frost-like etch-figures are produced on the surface (*tin-moirée*). When tin is bent, a peculiar crackling sound (cry of tin) is heard, which is probably caused by the grating of the crystal faces on each other. Tin is very malleable and ductile; it can be beaten into very thin leaves (*tin-foil*) at the ordinary temperature, and at  $100^\circ$  it can be drawn out into wire. At a very low temperature, quickest at  $-48^\circ$  and in contact with an alcoholic pink-salt solution (§ 201), tin passes spontaneously into another modification, *gray tin*, which has a lower specific gravity, 5.8. Above  $20^\circ$  this form changes back to white tin. If the latter is brought in contact with gray tin at ordinary temperatures (below  $+20^\circ$ ), it turns very slowly into gray tin, falling to powder (this phenomenon is called the tin-pest). If it is not in contact with the gray modification, the transformation does not take place at all at ordinary temperatures, or at least not

for centuries. Evidently there is a transition-point of the two forms at 20°, and we are forced to the odd conclusion that, except on warm summer days, all the tin in the world is in the metastable condition (§ 237).

At 200° it is brittle and can be easily pulverized. This is probably due to still another allotropic form.

*Chemical Properties.*—Tin is unaffected by the air at ordinary temperatures; if heated strongly, it burns with an intense white light to tin oxide, SnO<sub>2</sub>. Hydrochloric acid dissolves it, forming stannous chloride and hydrogen. It is also attacked by nitric acid (§ 201). A boiling solution of caustic soda or potash converts it into a stannic acid salt (s t a n n a t e) with the evolution of hydrogen:



In the presence of weak acids (acetic acid) and alkalies it is very stable.

**199. Uses.**—On account of its permanence tin is used as a protective covering for metals which are attacked by the air and the above-named agencies. Many kitchen utensils are “tinned.” Sheet iron is covered with a layer of tin, to protect it from rusting (§ 280), and is then known as *tin plate*, or *sheet tin*. This is done by simply dipping the sheet iron, which has been cleaned by hydrochloric or sulphuric acid, in molten tin.

Many **alloys** of tin are in use. *Solder* consists of tin and lead (in the ratio 2:1 or 1:1 or 1:2), and is harder than either of its components but more easily fusible. The alloys of copper and tin are called *bronzes*; their composition varies according to the purpose they serve. At present the bronzes usually contain a little lead and zinc as well. Bronze is hard and tough, can be easily worked and fuses to a mobile liquid, hence it is particularly suitable for casting. *Gun metal* contains 90% copper and 10% tin; *bell metal* 20–25% tin, the rest being copper. *Phosphorus bronze* is prepared by fusing copper with tin phosphide (§ 202). The resulting mass is remarkably homogeneous and contains 0.25–2.5% phosphorus and 5–15% tin. Its great hardness and firmness render it especially valuable for certain parts of machines (axle-bearings). *Silicon bronze* contains silicon in place of phosphorus, is very hard and conducts electricity well, hence it is used for making telephone wire. *Tin amalgam* forms the metallic coating of mirrors.

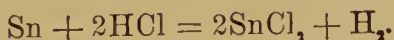


## Compounds of Tin.

Tin forms two sets of compounds; they correspond to the oxygen compounds, *stannous oxide*,  $\text{SnO}$ , and *stannic oxide*,  $\text{SnO}_2$ .

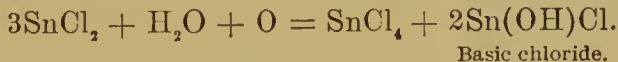
## STANNOUS COMPOUNDS.

200. **Stannous chloride**,  $\text{SnCl}_2$ , is prepared by dissolving tin in hydrochloric acid:



It crystallizes with two molecules of water, which are given off at  $100^\circ$ . It is very readily soluble in water (1 part in 0.37 at ordinary temperatures). Anhydrous stannous chloride is white and transparent; it melts at  $250^\circ$  and boils at  $606^\circ$ . A little above the boiling-point the vapor density corresponds to the formula  $\text{Sn}_2\text{Cl}_4$ ; above  $900^\circ$ , however, to  $\text{SnCl}_2$ .

The aqueous solution acts strongly reducing. It absorbs oxygen from the air with the partial formation of basic chloride (a white powder), if the liquid is not too acidic:



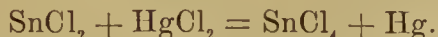
But, if the liquid is strongly acid, the tetrachloride  $\text{SnCl}_4$  is also formed in this oxidation.

This same basic chloride also results from hydrolytic dissociation, when a neutral stannous chloride solution is strongly diluted.



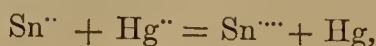
The reducing power of stannous chloride is farther seen in its action on potassium permanganate, potassium bichromate, cupric chloride, mercuric chloride, etc., all of which are converted into lower stages of oxidation in acid solution.

It may be remarked here that, from the ionic point of view, oxidation amounts in many cases to raising an ion to a higher positive potential, and reduction to the reverse. Let us consider, for instance, the reaction between stannous chloride and mercuric chloride. This can be expressed by the equation:



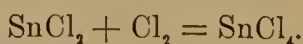
Stannous chloride is oxidized to stannic chloride; at the same time

mercuric chloride is "reduced" to the metal. Written in ions, this equation becomes

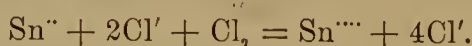


that is, the electrical charge of the mercury ion is taken by the bivalent tin ion, the former losing its electrification.

Another example is the action of chlorine on stannous chloride, by which the latter is "oxidized" to stannic chloride:

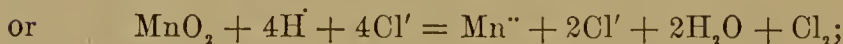


The ionic reaction is



Tin takes up two more positive charges, but this necessitates that the two Cl-atoms become ions; they thus require two negative charges; but when these are formed two positive charges are obtained at the same time.

In the preparation of chlorine, hydrochloric acid is "oxidized" by manganese dioxide:



the positive charge of the four H<sup>+</sup>-ions is thus transferred, half to the manganese and the rest serving to discharge two chlorine ions, i.e. to equalize their negative charges.

Various *double salts* of stannous chloride are known, e.g.  $\text{SnCl}_2 \cdot 2\text{KCl}$ ;  $\text{SnCl}_2 \cdot 2\text{NH}_4\text{Cl}$ .

**Stannous hydrate**,  $\text{Sn}(\text{OH})_2$ , is precipitated when a solution of stannous chloride is treated with soda:



This hydroxide is insoluble in ammonia, but soluble in alkalies; when the latter solution is boiled, tin is deposited and alkali stannate, e.g.  $\text{K}_2\text{SnO}_3$ , formed. The hydrate is also soluble in acids, thus displaying a basic as well as an acidic nature. **Stannous oxide** is obtained by heating the hydroxide in a current of car-

bon dioxide; it is a dark-brown powder, which takes fire in the air, burning to stannic oxide,  $\text{SnO}_2$ .

Other salts of stannous oxide than the above-mentioned stannous chloride are also known. The sulphate, for instance, is obtained by dissolving the hydrate or the metal in dilute sulphuric acid. It forms a basic salt readily.

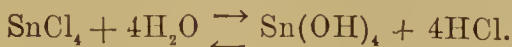
**Stannous sulphide**,  $\text{SnS}$ , falls down as an amorphous brown powder when hydrogen sulphide is passed into the solution of stannous salts. It is insoluble in potassium sulphide,  $\text{K}_2\text{S}$ . Nevertheless, it dissolves to form a sulpho-stannate, when brought in contact with the polysulphide of ammonium or potassium,  $\text{K}_2\text{S}_x$  ( $x = 2-5$ ).



Stannous sulphide can also be prepared by fusing tin with sulphur. It then forms a bluish-gray crystalline mass.

#### STANNIC COMPOUNDS.

**201. Stannic chloride**,  $\text{SnCl}_4$ , was prepared as early as 1605. It was named *spiritus fumans Libavii* after its discoverer. It is obtained by the action of chlorine on tin or stannous chloride. Stannic chloride is a liquid which fumes strongly in the air; it boils at  $113.9^\circ$ , and has a specific gravity of 2.234 at  $15^\circ$ . When brought in contact with a little water or on taking up moisture from the air, it goes over into a semi-solid, crystallized mass,  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ , the so-called *tin-butter*. A fresh solution of stannic chloride is a very poor conductor of electricity. However, the conductivity increases slowly at ordinary, faster at higher, temperatures; after several days it reaches a maximum. In the case of more dilute solutions this maximum is much higher. These facts can only be explained by assuming that the  $\text{SnCl}_4$  molecule is not capable of ionization, but that it reacts with water in the following way :



It is the liberated hydrochloric acid that causes the conductivity. The solution contains tin hydroxide in the colloidal state. The water has thus split up stannic chloride into a basic hydroxide and

an acid. We shall meet with still more examples of such a reaction, which is called a **hydrolysis** (see § 239).

Stannic chloride forms well-crystallized double-salts with the alkali chlorides, e.g.  $\text{SnCl}_4 \cdot 2\text{KCl}$  and  $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$ . The latter is known as *pink salt* (because of its color) and is used as a mordant in dyeing. Tin tetrachloride also unites with the chlorides of the metalloids to form crystallized substances, e.g.  $\text{SnCl}_4 \cdot \text{PCl}_5$ ;  $\text{SnCl}_4 \cdot \text{POCl}_3$ ;  $\text{SnCl}_4 \cdot \text{SCl}_4$ , etc. It combines with hydrochloric acid, forming a leafy-crystalline mass,  $\text{H}_2\text{SnCl}_6 \cdot 6 \text{aq}$ , which melts at  $9^\circ$ .

**Tin fluoride**,  $\text{SnF}_4$ , itself is not known, but there is a compound,  $\text{K}_2\text{SnF}_6$ , which corresponds to potassium fluo-silicate; the salts of hydrofluostannic acid are isomorphous with the analogous silicon compounds.

**Stannic oxide**,  $\text{SnO}_2$ , can be prepared synthetically by heating tin in the air. It is an amorphous white powder, insoluble in acids and alkalies; the latter, however, dissolve it, when fused, forming stannates.

**Stannic Acid and Metastannic Acid.**—The hydroxides corresponding to  $\text{SnO}_2$  have only very weakly basic properties; here the acidic properties are prominent. The normal hydrate,  $\text{Sn}(\text{OH})_4$ , is unknown, but there is a hydrate of the empirical composition  $\text{H}_2\text{SnO}_3 (= \text{Sn}(\text{OH})_4 - \text{H}_2\text{O})$ , corresponding to carbonic acid,  $\text{H}_2\text{CO}_3$ . Strangely enough this exists in two modifications, which differ from each other both chemically and physically; they are called stannic and metastannic acids.

The **stannic acid** is precipitated when ammonia is added to an aqueous solution of stannic chloride or hydrochloric acid to a potassium stannate solution. This precipitate reacts acid when moist and is soluble in concentrated hydrochloric and nitric acids, as well as in alkalies. It gradually changes into metastannic acid.

**Metastannic acid** is generally prepared by treating tin with strong nitric acid; it is then formed in a vigorous reaction as a dense white powder. Metastannic acid is insoluble in sodium hydrate, but nevertheless unites with it to form sodium metastannate; this is dissolved by water, albeit with difficulty, but is insoluble in the caustic soda solution. When boiled with hydrochloric acid, metastannic acid goes over into a chloride, which is insoluble in the concentrated acid but soluble in water. This solution does not contain the ordinary tin chloride, but another one, *meta-tin chloride*, having, however, the same composition,  $\text{SnCl}_4$ . It is

distinguished from the ordinary stannic chloride by giving a yellow coloration with stannous chloride solution; the solution of the ordinary chloride does not do this till after some time, during which the metachloride is formed in it.

Stannic acid and the corresponding chloride thus pass over into the meta-compounds spontaneously; on the other hand, metastannic acid can be converted into the ordinary tin compounds by boiling it for some time or fusing it with a caustic alkali.

The difference between stannic and metastannic acids was set forth by BERZELIUS as early as the beginning of the nineteenth century; nevertheless we are still without a satisfactory explanation of the matter. Inasmuch as the salts of metastannic acid, however, have in general a very complicated composition, similar to the polysilicates (§ 195), it is probable that metastannic acid is a polymer of the ordinary stannic acid, i.e. that its molecule is represented by  $(\text{H}_2\text{SnO}_3)_x$ , stannic acid itself being  $\text{H}_2\text{SnO}_3$ .

Of the salts of stannic acid, the sodium stannate,  $\text{Na}_2\text{SnO}_3 + 3\text{H}_2\text{O}$ , is especially well known. It comes on the market under the name of "preparing-salt" and is used as a mordant in dyeing. It is made by fusing tin-stone with caustic soda and crystallizes in hexagonal crystals, which are more soluble in cold than in warm water.

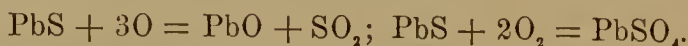
**202. Stannic sulphide**,  $\text{SnS}_2$ , falls out as a yellow amorphous powder, when hydrogen sulphide is passed into the acid solution of a stannic compound. It can be synthesized by heating tin amalgam with sulphur and ammonium chloride, being thus obtained in the form of transparent golden leaves and known as *aurum musivum*, or *mosaic gold*; it is used for gilding. Stannic sulphide is a sulpho-anhydride; the corresponding sulpho-acid,  $\text{H}_2\text{SnS}_3$ , is not known in the free state, but exists in the form of salts.

**Sodium sulphostannate**,  $\text{Na}_2\text{SnS}_3 + 2\text{H}_2\text{O}$ , crystallizes in colorless octahedrons. When its solution is treated with an acid, stannic sulphide is precipitated.

**Tin phosphide** serves, as was stated above, for the manufacture of phosphorus bronze. Of the various compounds of tin and phosphorus the best known is the compound  $\text{Sn}_3\text{P}$ . It forms a coarsely crystalline mass, which melts at  $170^\circ$ .

## LEAD.

203. Among the lead ores the most important is *galenite* (PbS); it occurs in regular crystals (cubes) of a graphitic color. Other ores are *cerussite* (PbCO<sub>3</sub>), *crocoite* (PbCrO<sub>4</sub>), *wulfenite* (PbMoO<sub>4</sub>), etc. For the extraction of the metal galcnite is used almost exclusively. This is roasted to convert the sulphide partially into oxide, and partially into sulphate:



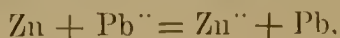
In roasting care is taken that a considerable portion of the ore remains as sulphide. On farther heating, the latter reacts with the oxygen compounds in the following way:



*Physical Properties.*—Lead is a soft ductile metal of a bluish color. On exposure to the air it loses its lustre rapidly, becoming coated with a very thin layer of oxide. It has a specific gravity of 11.254, melts at 334°, and at white heat distills.

*Chemical Properties.*—The thin coating formed by the oxide on the brilliant surface of the metal protects the lead from further attack by the air. If, however, it is prepared in a very finely divided state, e.g., by heating lead tartrate or citrate in the absence of air, it takes fire in the air even at ordinary temperatures. This is called *pyrophorus*. (Other metals also can take on this same condition when they are reduced in a similar way to such a fine state of division.) When lead is melted, it becomes coated with red oxide of lead; by constantly removing the latter, the lead can be entirely oxidized. A compact mass is unaffected by sulphuric or hydrochloric acid, but, when finely divided, it reacts to form the corresponding salts. Nitric acid easily dissolves it to form the nitrate. Acetic acid and various vegetable acids attack it; since all lead salts are very poisonous and very serious effects result from chronic poisoning with insignificant but successive amounts, it is not admissible to use tin containing lead in tin-plating vessels for use in the kitchen.

Zinc and iron precipitate the metal from solutions. A piece of zinc becomes covered with a dendritic crystalline mass ("lead tree"). This reaction can be expressed by :



i.e. zinc is changed into the ionic condition, and the lead ions are discharged. How it comes about that one metal thus assumes the electrical charge of another may be explained by a hypothesis of NERNST. His supposition is that every metal on coming in contact with water or a solution tends to send positive ions into it. The force, however, with which this *electrolytic solution-tension* asserts itself differs greatly for different metals; it is much larger for zinc than for lead. Thus, when a piece of zinc is introduced into solution containing lead ions, zinc ions are forced into the solution, the piece of zinc itself assuming a negative charge. The lead ions are now able to discharge themselves on the piece of zinc, and, as they are not driven back into the solution with the same force as the zinc ions, the result must be that all the lead ions disappear and are replaced by zinc ions (see also § 276).

Distilled water, from which the air has been entirely removed by boiling, has no effect on lead, but the simultaneous action of air and water produce lead hydroxide, which is somewhat soluble in water. This hydroxide is converted into insoluble basic carbonate by carbonic acid.

From a hygienic standpoint these properties of lead are of vast importance, because drinking-water is quite universally conducted through pipes made of lead or material containing lead ("compo-pipes"). The absorption of lead from such pipes by water and the continuation of the process depends in a large measure on the proportion of salt in the water. As a rule, the less of salts it contains, the more lead it takes up. Rain-water, which is almost entirely free from solid matter, but contains oxygen, carbon dioxide and traces of ammonia, is, therefore, most likely to dissolve lead. The lead eave-troughs, etc., which were once extensively used, should, therefore, be rejected, in case the rain-water is used for drinking. Well-water usually contains acid calcium carbonate and gypsum; as a result, the lead pipes soon become coated with an insoluble layer of lead sulphate and basic carbonate (as well as calcium carbonate), so that after a while the lead can no longer be absorbed by the water.

Lead is used for many purposes, not only in the elemental condition, but also in the form of alloys (see § 199).

### Oxides of Lead.

204. The following oxides of lead are known:  $Pb_2O$ ,  $PbO$ ,  $Pb_2O_3$ ,  $Pb_3O_4$ ,  $PbO_2$ .

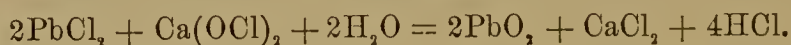
Lead suboxide,  $Pb_2O$ , is a velvet-black powder, which readily turns to lead oxide on heating in the air.

**Lead oxide**,  $\text{PbO}$ , is the only one of these oxides with basic properties. It is formed by direct synthesis from its elements (§ 203). It is fusible, and congeals again to a reddish-yellow mass called *litharge*. By carefully heating lead, lead hydroxide or lead nitrate, the oxide is obtained as an amorphous brown powder (*massicot*). It is somewhat soluble in water, forming the hydroxide. It dissolves in caustic potash, and crystallizes out in rhombic prisms on cooling.

**Lead hydroxide**,  $\text{Pb}(\text{OH})_2$ , is formed by precipitating a lead solution with an alkali. It is soluble in caustic alkalies, but insoluble in ammonia. On being warmed to  $145^\circ$  it gives up water and turns to oxide. It is somewhat soluble in water, imparting to the latter an alkaline reaction, and absorbs carbon dioxide from the air.

**Minium**,  $\text{Pb}_3\text{O}_4$ , is prepared by heating lead oxide or white lead in the air for quite a while at  $300\text{--}400^\circ$ . It has a pretty red color, and is therefore used as a pigment in painting. Gentle heating makes the color a brighter red at first; stronger heating turns it violet and finally black; on cooling, however, the original color returns. By treating it with dilute nitric acid, lead nitrate and lead peroxide are formed, hence minium may be regarded as  $2\text{PbO} \cdot \text{PbO}_2$ .

**Lead peroxide**,  $\text{PbO}_2$ , is obtained in the way just stated; more easily, however, by passing chlorine into an alkaline lead solution or adding a hypochlorite to a lead salt, thus:



Milk of lime is then added to form a salt of the free acid.

Lead peroxide is an amorphous dark-brown powder. It has the property, common to most peroxides, of giving up oxygen easily. At an elevated temperature it splits up into lead oxide and oxygen. On warming it with sulphuric acid, lead sulphate and oxygen are formed; on warming with hydrochloric acid, lead chloride and chlorine are produced.

Lead peroxide, like  $\text{CO}_2$  and  $\text{SnO}_2$ , has the character of an acid anhydride; it is soluble in hot concentrated potassium hydrate and this solution, on cooling, deposits crystals of the composition  $\text{K}_2\text{PbO}_3 + 3\text{H}_2\text{O}$  (which are thus entirely analogous in composition to potassium stannate). This *plumbate* is easily decomposed by



water into potassium hydrate and lead peroxide. If we regard lead peroxide as an acid anhydride, minium can be considered as the lead salt of the normal plumbic acid,  $\text{Pb}(\text{OH})_4$ , i.e.  $\text{Pb}_2 \cdot \text{PbO}_4$ . This idea is confirmed by the following method of formation: If a solution of lead oxide in potassium hydrate is added to a solution of the plumbate  $\text{K}_2\text{PbO}_3$ , a yellow substance is precipitated having the composition  $\text{Pb}_3\text{O}_4 \cdot \text{H}_2\text{O}$ , which gives off water readily and forms minium.

If a mixture of litharge and calcium carbonate is heated in a current of air at  $700^\circ$ , carbon dioxide is given off, oxygen absorbed and calcium plumbate,  $\text{CaPbO}_3$ , formed. If this plumbate is treated with carbon dioxide at about the same temperature, calcium carbonate and lead oxide are again formed, while oxygen escapes. This process (discovered by KASSNER) serves for the commercial manufacture of oxygen. The latter is brought on the market compressed in iron bottles (*cf.* also § 262).

The oxide  $\text{Pb}_2\text{O}_3$  is obtained by adding sodium hypochlorite to a solution of lead oxide in potassium hydrate. It can be regarded as the lead salt of a lead acid,  $\text{H}_2\text{PbO}_3$ , i.e. as  $\text{Pb} \cdot \text{PbO}_3$ , for, on treatment with dilute nitric acid  $\text{PbO}$  (the anhydride of  $\text{H}_2\text{PbO}_3$ ) and lead nitrate are formed.

### Halogen Compounds.

205. The halogen compounds of lead having the formula  $\text{PbX}_2$  are difficultly soluble in cold water; lead fluoride is almost insoluble and the solubility of the three others decreases with increasing atomic weight of the halogen.

Lead chloride,  $\text{PbCl}_2$ , is obtained as a white precipitate when dilute hydrochloric acid is added to the solution of a lead salt. At  $12.5^\circ$  it dissolves in 135, at  $100^\circ$  in less than 30, parts of water and crystallizes from the hot solution in the form of white silky needles or lamellæ. If an aqueous solution of lead chloride is treated with dilute hydrochloric acid, lead chloride is precipitated, for by the addition of  $\text{Cl}^-$  ions the solubility product of lead chloride is exceeded; nevertheless, lead chloride is easily soluble in concentrated hydrochloric acid. This must be due to the formation of a compound of the chlorides of lead and hydrogen, an analogue of which has been found in  $\text{PbI}_2 \cdot \text{HI} + 10\text{H}_2\text{O}$ , which has been isolated. A characteristic compound of lead is the iodide  $\text{PbI}_2$ , which is precipitated from lead solutions by potassium iodide. It is scarcely

soluble in cold, moderately soluble in hot water. It crystallizes out of a solution in dilute acetic acid in beautiful crystal flakes with a golden lustre.

**Lead tetrachloride**,  $\text{PbCl}_4$ , is formed when a solution of lead dichloride in strong hydrochloric acid is saturated with chlorine. From this liquid ammonium chloride precipitates a lemon-yellow crystalline substance,  $2\text{NH}_4\text{Cl} \cdot \text{PbCl}_4$ , having a composition analogous to pink salt (§ 201).

### Other Lead Salts.

**206. Lead nitrate**,  $\text{Pb}(\text{NO}_3)_2$ , is obtained by dissolving lead in dilute nitric acid. It is colorless, crystallizes isometric (regular) and is soluble in 8 parts of water. Heating decomposes it (§ 122). Several basic lead nitrates are known.

**Lead sulphate**,  $\text{PbSO}_4$ , is practically insoluble in water and can therefore be obtained by precipitating a lead solution with dilute sulphuric acid or a soluble sulphate. It occurs as a mineral in crystallized form under the name of *anglesite*; it is isomorphous with the sulphate of barium, barite. Lead sulphate is soluble in concentrated sulphuric acid; hence the crude acid which is concentrated in lead pans (§ 186, 3) contains lead sulphate; this is precipitated on diluting the acid with water. It is dissolved by concentrated alkalis. Ignition with charcoal easily reduces it to sulphide.

**Lead persulphate**,  $\text{Pb}(\text{SO}_4)_2$ , can be obtained by the electrolysis of strong sulphuric acid (sp. g. 1.7–1.8) between electrodes of lead. The salt separates from the acid around the anode. It has not been obtained quite free from lead sulphate. It is a white granular substance. Water decomposes it readily into sulphuric acid and lead peroxide. It has strong oxidizing properties.

**Lead carbonate**,  $\text{PbCO}_3$ , is deposited when a solution of the nitrate is treated with ammonium carbonate. *White lead*, a basic carbonate, is used extensively as a pigment. However, it soon turns black, if any hydrogen sulphide (from drainage pipes, etc.) comes in contact with it; moreover, it is injurious to the health, because it comes off of the painted walls in the form of dust and gets into the lungs. White lead is particularly valuable for its *covering-power*, i.e. the painted surface appears perfectly white when covered with only a very thin layer of the pigment; it is much greater than that of other white pigments, such as white zinc

and barite, which are frequently substituted for white lead because they are harmless.

The manufacture of white lead is still carried on extensively after the Dutch method. This consists in placing rolls or "buckles" of lead plate into jars containing a little acetic acid. The vessels are loosely covered with a leaden lid and buried in a heap of horse-manure. The heat generated by the decaying manure causes a part of the acetic acid to evaporate and converts the lead into basic lead acetate. The latter is then transformed to white lead by the carbon dioxide given off from the decaying heap. After about five or six weeks the plates are almost entirely changed to white lead. This is then ground moist, washed out (to remove any acetate) and dried, whereupon it is sent to the market.

Lead sulphide,  $PbS$ , is black and comes down amorphous when hydrogen sulphide is passed into a lead solution. A liquid containing only traces of lead is colored brown by sulphuretted hydrogen; this is a very delicate means of testing for lead. Strong nitric acid oxidizes it readily to lead sulphate.

### SUMMARY OF THE CARBON GROUP.

207. The elements *carbon, silicon, germanium, tin* and *lead* form a natural group, as may be seen from a comparison of their physical and chemical properties. In the following small table the most important physical constants are summarized; here, as in other natural groups, the gradual change of these constants with the rise of the atomic weight is very manifest:

	C.	Si.	Ge.	Sn.	Pb.
Atomic weight.	12.00	28.4	72	118.5	206.9
Specific gravity	{ 2.25 } { 3.6 }	2.49	5.5	7.29	11.39
Melting-point..	.....	very high	circa 900°	233°	334°
Boiling-point...	above 3000°	.....	.....	circa 1500°	circa 1600°

With respect to the chemical properties we note in the first place that all these elements have the same compound types,  $MX_2$  and  $MX_4$ ; in other words, that they are bi- or quadri-valent; this is even true of lead ( $PbO_2$ ,  $PbCl_4$ , etc.), which does not fit into the table of physical properties with its boiling- and melting-points.

Moreover, there is to be noted in general a transition from metalloid to metallic character, as is plainly shown by the following facts:

1. Only carbon and silicon are known to form hydrogen compounds (of an indifferent nature).

2. Of the oxygen compounds of the MO type, that of carbon is indifferent and the others (no such compound of silicon is known) grow more basic in character as the atomic weight increases, lead hydroxide having quite strongly alkaline properties.

3. The oxygen compounds,  $RO_2$ , however, are decidedly acidic in character in the cases of carbon and silicon and also in the case of germanium, while in that of lead the salts of the acid  $H_2PbO_3$  are immediately decomposed by water, so that here the acid properties appear much weakened.

4. As to the halogen compounds, those of carbon ( $CX_4$ ) are unaffected by cold water—perhaps because of their insolubility in it; the other halogen compounds,  $MX_4$  are decomposed by water.

Lead, in some of its physical and chemical properties, does not display the gradation which is ordinarily met with in the elements of a group. This phenomenon is quite often observed in elements of very high atomic weight. In the nitrogen group we saw it in the case of bismuth.

### METHODS OF DETERMINING ATOMIC WEIGHTS.

**208.** So far only one method of determining the atomic weight has been mentioned (§ 34). This consists in investigating as large as possible a number of gaseous compounds of the element as to their vapor density and empirical composition and then calculating how many grams of the element are contained in a gram-molecule of the various compounds. This method is quite general.

There are, however, other methods. None of them are so generally applicable as this, but they have been of great value in the many cases in which they could be used. They furnish a very valuable check on the determinations made by the general method. These methods are based on the following laws :

1. The law of **DULONG** and **PETIT**. *The product of the atomic weight of a solid element and its specific heat is about 6.4.* This follows from the table opposite.

Element.	Sp. H.	At. Wt.	Prod- uct.	Remarks.
Hydrogen.....	5.880	1.01	5.9	Investigated in its Pd alloy (§ 315).
Lithium.....	0.941	7.03	6.6	
Beryllium.....	0.408	9.1	3.7	Sp. H. at 257° = 0.58; prod. = 5.2.
Boron.....	0.254	11	2.8	Amorphous. Sp. H. at 400° = 0.58; prod. = 6.4.
Carbon { amorphous	0.174	{ 12.00 }	2.1	Above 900° Sp. H. = 0.459; prod. = 5.5.
{ diamond..	0.143		1.76	
Sodium.....	0.293	23.05	6.7	
Magnesium.....	0.250	24.36	6.1	
Aluminium.....	0.214	27.1	5.8	
Silicon.....	0.165	28.4	4.6	Crystallized. Sp. H. above 200° = 0.204; prod. = 5.8.
Phosphorus.....	0.189	31.0	5.9	Yellow. Sp. H. of red P = 0.1698; prod. = 5.24. Rhombic.
Sulphur.....	0.178	32.06	5.7	
Potassium.....	0.166	39.15	6.5	
Calcium.....	0.170	40.0	6.8	
Scandium.....	0.153	44.1	6.7	
Chromium.....	0.121	52.1	6.3	
Manganese.....	0.122	55.0	6.7	
Iron.....	0.114	56.0	6.4	
Cobalt.....	0.107	59.0	6.3	
Nickel.....	0.108	58.7	6.4	
Copper.....	0.095	63.6	6.0	
Zinc.....	0.094	65.4	6.1	
Gallium.....	0.079	70	5.5	
Germanium.....	0.077	72	5.6	
Arsenic.....	0.082	75	6.9	Crystallized.
Selenium.....	0.080	79	6.3	Do.
Bromine.....	0.084	79.96	6.7	Solid.
Zirconium.....	0.066	90.7	6.0	
Molybdenum.....	0.072	96.0	6.9	
Ruthenium.....	0.061	101.7	6.3	
Rhodium.....	0.058	103.0	6.0	
Palladium.....	0.059	106	6.0	
Silver.....	0.057	107.93	6.1	
Cadmium.....	0.054	112.4	6.0	
Indium.....	0.057	114	6.5	
Tin.....	0.054	118.5	6.5	
Antimony.....	0.051	120	6.1	
Tellurium.....	0.047	127	6.0	
Iodine.....	0.054	126.85	6.8	
Lanthanum.....	0.045	138.0	6.2	
Cerium.....	0.045	140	6.3	
Tungsten.....	0.033	184	6.1	
Osmium.....	0.031	191	5.9	
Iridium.....	0.032	193.0	6.1	
Platinum.....	0.032	194.8	6.2	
Gold.....	0.032	197.2	6.3	
Mercury.....	0.032	200.3	6.4	Solid.
Thallium.....	0.033	204.1	6.7	
Lead.....	0.031	206.9	6.4	
Bismuth.....	0.030	208.5	6.2	
Thorium.....	0.027	232.5	6.2	
Uranium.....	0.027	239.5	6.5	

Most of the values of the product lie, as the table shows, very close to 6.4; the maximum is 6.9, the minimum 5.0. Calling this product the **atomic heat**, we can express the law of DULONG and PETIT in the following simple way: *The atomic heat of the solid elements is approximately constant and is about 6.4.*

A few deviations have been pointed out in the last column; in such cases it has frequently been found, however, that at an increased temperature the atomic heat approaches the value 6.4. This is probably due to the fact that at the temperature (room-temperature) at which the measurements of the specific heat of the elements have been mainly carried out, the elements are not all in the proper physical condition for comparison. It is notably the elements with atomic weights under 35 that show the greatest deviations.

It is an interesting fact that there is a certain regularity to be found in these irregularities. The latter become more marked as the valence increases.

Element.....	Li	Be	B	C	Na	Mg	Al	Si	P	S
Valence.....	1	2	3	4	1	2	3	4	3(5)	2(4,6)
Atomic heat.....	6.6	3.7	2.8	1.9	6.7	6.1	5.8	4.6	5.9	5.7

It is easy to see how the law of DULONG and PETIT can be made use of for the determination of atomic weights. Inverting,

$$\text{we have } \frac{6.4}{\text{Sp.H.}} = \text{At. wt.}$$

Of course the result thus obtained is only approximately correct, for the product 6.4 is not strictly constant. The method is, however, reliable enough to determine what multiple of the equivalent weight (§ 23), the exact value of which can be found by analysis, is the atomic weight.

**209. 2.** Closely connected with the law just enunciated is that of NEUMANN, which has been more carefully investigated by REGNAULT and KOPP. This law says that *in solid compounds each element has a constant atomic heat, which varies but little from that of the free element.* The molecular heat is therefore equal to the sum of the atomic heats. If the molecular heat of solid compounds is divided by the number of atoms, the quotient must be about 6.4. In reality this quotient proved to be: for bromine compounds RBr, 6.9; for RBr<sub>2</sub>, 6.5; for iodine compounds RI, 6.7; RI<sub>2</sub>, 6.5. The law of NEUMANN likewise holds for many elements whose specific

heat in the solid state has not been possible to determine, thus e.g. for chlorine compounds: for RCl compounds the quotient referred to was 6.4, for RCl<sub>2</sub>, 6.2, for certain double chlorides, 6.1–6.2. For other elements like oxygen, the atomic heat found from the molecular heat of the compounds is constant, but it is about 4.0 instead of about 6.4. The same is true of hydrogen, whose mean atomic heat in solid compounds is 2.3. These figures were found by determining the molecular heat of various oxygen or hydrogen compounds and subtracting from it the known atomic heats of the other elements. If the atomic heat thus obtained is divided by the atomic weight, we have the specific heat of the element in its compounds.

The way in which the law of NEUMANN can be applied to atomic weight determinations is illustrated by the following example:

The problem is to determine the atomic weight of calcium with the help of the specific heat of sulphate of lime, CaSO<sub>4</sub>, which amounts to 0.1966 according to REGNAULT.

Analysis has shown that 1 kg. anhydrous calcium sulphate contains 0.294 kg. calcium, 0.235 kg. sulphur and 0.471 kg. oxygen. The atomic heat of oxygen in compounds is 4.0 (see above), and, since its atomic weight is 16, the specific heat of oxygen in its compounds is  $\frac{4.0}{16} = 0.25$ . In the same manner it is found that the specific heat of sulphur in compounds is  $\frac{5.4}{32} = 0.169$ .

The heat-capacity of 0.235 kg. sulphur in compounds is therefore

$$0.235 \times 0.169 = 0.0397$$

The heat-capacity of 0.471 kg. oxygen in compounds is.....

$$0.471 \times 0.25 = 0.1177$$

Total.....

$$\underline{0.1574}$$

This sum subtracted from the specific heat of anhydrous calcium sulphate (0.1966) gives the heat-capacity of 0.294 kg. calcium: hence the latter is

$$0.1966 - 0.1574 = 0.0392.$$

The specific heat of calcium in its compounds is therefore

$$\frac{0.0392}{0.294} = 0.133.$$

The atomic heat of calcium as a metal, we may assume with great prob-

ability, is not far from 6.4. The atomic weight will therefore amount to about  $\frac{6.4}{0.133} = 48$ .

Now the equivalent weight of calcium is known from the analysis of calcium chloride; it is 20.0, since 35.45 parts by weight of chlorine are in combination with 20 parts of calcium. The atomic weight must therefore be this number or a simple multiple of it; evidently twice the equivalent weight, or 40.0, is the nearest of all the multiples to the number 48, so that 40.0 must be taken as the atomic weight.

The value of the atomic weight calculated from NEUMANN'S law therefore serves merely to decide what multiple of the equivalent weight must be taken; for this purpose the number so obtained is sufficiently accurate.

**210. 3. The law of MITSCHERLICH.** *The crystal form of compounds having analogous chemical composition is the same; or, in other words, compounds of analogous chemical composition are isomorphous.* The compounds KCl, KI, KBr, e.g. are analogous in composition; they all crystallize in cubes.  $\text{H}_2\text{KPO}_4$ ,  $\text{H}_2\text{KAsO}_4$ ,  $\text{H}_2(\text{NH}_4)\text{PO}_4$  also have an analogous composition and all crystallize in the tetragonal system. The analogous compounds  $\text{KClO}_4$  and  $\text{KMnO}_4$  both crystallize rhombic.

If two compounds have been proven to be isomorphous, it is very probable that their composition is analogous, whereupon the atomic weight is readily found. Let us, for example, take the case of manganese, supposing its atomic weight to be unknown; now potassium permanganate is isomorphous with potassium perchlorate, which latter is known to have the formula  $\text{KClO}_4$ . Analysis has shown the formula of potassium permanganate to be  $\text{KMn}_x\text{O}_4$ ,  $x$  being unknown, for 39 parts (by weight) of potassium (1 atom) are combined with 64 parts of oxygen (4 atoms) and 55 parts of manganese ( $x$  atoms). From its isomorphism with  $\text{KClO}_4$  it follows that its formula must be  $\text{KMnO}_4$  (i.e.  $x = 1$ ), hence 55 is the atomic weight of manganese.

In determining the atomic weight of zinc we could use the isomorphism of the crystallized sulphates of magnesium and zinc. The formula of the former is  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ . On the basis of the analysis of zinc sulphate and the isomorphism mentioned we have the formula  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ , from which the atomic weight is obtained in the same way as above.



The law of isomorphism was discovered as early as 1819. Since at that time the law of AVOGADRO received little attention and the determination of the specific heat was in many cases impossible, the phenomena of isomorphism were the most important means of getting information regarding the value of the atomic weight. Subsequently its importance for this purpose lessened, mainly because simpler means were found, but also because it proved to be very difficult in many cases to decide whether two substances are isomorphous. Moreover it was found that certain substances of entirely different composition are isomorphous.

For the **determination of isomorphism** the following methods are now in use :

1. The determination of the crystal form. Measurements have shown that this is almost never *exactly* the same for substances of unquestioned isomorphism, hence it is very difficult to fix a limit beyond which two crystals shall not be considered alike. Again, the form of the crystals can be apparently exactly the same, while nevertheless no isomorphism exists, because one crystal is hemihedral and the other holohedral. This is the case, e.g., with potassium and sodium chloride, which for a long time were incorrectly considered isomorphous. There are, however, various methods of detecting this difference in symmetry, e.g. by means of etch-figures; when the smooth faces are moistened with a liquid which acts on the substance of the crystal, characteristic lines or figures are produced. If these etch-figures are the same for two crystals, which otherwise agree in form, the two have the same degree of symmetry.

2. Another characteristic of isomorphism is that isomorphous crystals have the ability to form mixed crystals, either in all proportions, or within certain limits inside of which all proportions are possible. Solutions containing two salts that crystallize isomorphous must yield crystals whose composition with respect to the two salts can vary in all proportions or at least in all proportions between certain limits. The formation of these mixed crystals is the most important evidence of isomorphism. It should be noted that between perfect miscibility on the one hand and absolute immiscibility on the other, all intermediate stages may occur, just as in the case of liquids, so that here also the limit is hard to fix in many cases.

3. A very delicate test for isomorphism, finally, is the fact that a supersaturated solution can be made to crystallize, not only by an extremely small amount of the dissolved substance itself ("sowing"), but by other bodies, that are isomorphous.

## THE PERIODIC SYSTEM OF THE ELEMENTS.

211. In studying the elements which we have considered so far, we have found that they can be arranged into groups of elements according to their valence, the elements of each showing great

similarity in the types of their compounds. The physical and chemical properties of the elements of such a group are found on the whole to gradually change as the atomic weight increases. The question now arises whether all elements can be thus arranged into groups; the reply is affirmative.

In the course of the last century there was no lack of attempts to arrange the elements into groups of similar elements. DOEBEREINER called attention to a simple relation between the atomic weights of kindred elements as early as 1817 and in 1829 he presented the doctrine of *triads*, i.e. he showed that there are different groups of three elements each, which have a great similarity among themselves and a constant difference in the atomic weights, e.g. Cl, Br, I; Ca, Sr, Ba, etc. In the year 1865 the *law of octaves* was proposed by NEWLANDS, he having discovered that, if the elements are arranged according to increasing atomic weight, after an interval of seven elements one follows which has properties analogous to those of the first, i.e. the first, eighth, fifteenth, etc., are similar. In 1869 MENDELÉEFF and LOTHAR MEYER almost simultaneously reached conclusions which are comprehended by the term "periodic system."

If we arrange the elements according to increasing atomic weight, thus:

							H 1	
Li 7	Be 9.1	B 11	C 12	N 14	O 16	F 19		
Na 23	Mg 24	Al 27.1	Si 28.4	P 31.0	S 32	Cl 35.4,		

we see that there is a *gradual* variation in the properties of elements in a horizontal line; after fluorine, however, a small increase in the atomic weight involves a *sudden* change of properties. Moreover those elements which are in the same vertical column show great similarity, as we saw above in the cases of carbon and silicon, nitrogen and phosphorus, etc.

This regular change makes itself evident in the valence toward oxygen, which rises from *one* (with Li and Na) to *two* (Be, Mg), *three* (B, Al), *four* (C, Si), *five* (N, P), *six* (S) and *seven* (Cl in  $\text{Cl}_2\text{O}_7$ ). The valence toward hydrogen or a halogen increases, however, from *one* (Li) to *four* (C) and then falls again to *one* (F). A similar regular change is to be observed with reference to the physical properties, e.g. specific gravity and atomic volume.

	Na	Mg	Al	Si	P (red)	S	Cl (liq.)
Sp. gravity.....	0.97	1.75	2.67	2.49	2.14	2.06	1.33
At. volume.....	24	14	10	11	14	16	27

By *atomic volume* we understand the atomic weight divided by the weight of the unit volume (based on water of 4° as 1); it is therefore the number of cubic centimeters occupied by a gram-atom.

Here we observe an increase of the specific gravity up to aluminium, then again a decrease to chlorine, while the atomic volume, on the other hand, decreases from the beginning of the series to aluminium and then increases. This steady change of the same physical properties is also observed in the compounds of the above elements. For the oxides, e.g. we have:

	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
Sp. gravity.....	2.8	3.7	4.0	2.6	2.7	1.9	?
At. volume.....	22	22	25	45	55	82	?

Moreover if we write down a series of elements according to increasing atomic weight beginning with another univalent metal, we discover regularities of exactly the same sort as the above. The following series may serve as an example of this:

	Ag	Cd	In	Sn	Sb	Te	I
Atomic wt.....	108	112.4	114	118.5	120	127	126.9
Sp. gravity.....	10.5	8.6	7.4	7.2	6.7	6.2	4.9

Here also we find the same gradual rise of valence from silver, which is univalent, to septivalent iodine, the progressive transition from metal to metalloid and a continuous decrease in specific gravity. But more; if we put this last row under the first two:

										H	1		
Li	7	Be	9.1	B	11	C	12	N	14	O	16	F	19
Na	23	Mg	24.4	Al	27.1	Si	28.4	P	31.0	S	32	Cl	35.5
Ag	108	Cd	112.4	In	114	Sn	118.5	Sb	120	Te	127	I	126.9

it is evident that the elements in the same vertical column belong to a group. This has been demonstrated for the last four columns in preceding chapters; it will be proven for the others later on.

In the light of these facts, we are led to the conclusion that *the physical and chemical properties of the elements are functions of their atomic weights*; and when we consider the series beginning with lithium and sodium, and note that in each instance, after a difference of about 16, there comes another element with corresponding properties, we are led to the supposition that these properties are *periodic* functions of the atomic weights.

By a **function** we understand in general a dependent relation between two or more magnitudes, of such a sort that, when one changes, the other does likewise. In the equations  $y = a \pm x$ ;  $y = ax$ ;  $y = x^n$ , etc.,  $y$  is a function of  $x$ , since, whenever  $x$  undergoes a change, the value of  $y$  also changes. A **periodic function** requires that the same value appear for one magnitude in regular intervals as the other magnitude steadily increases. An example of this kind is presented by the goniometric functions, as  $y = \sin x$ , etc., for every time  $x$  increases by  $2\pi$ ,  $y$  comes to have the same value again. The sudden transition in the series of elements from very strongly negative to very strongly positive, which occurs between the end of each period and the beginning of the succeeding one, reminds one of a tangential function  $y = \tan x$ , which changes from  $+\infty$  to  $-\infty$  for  $x = \frac{1}{2}\pi$ , etc.

If we desire to substantiate the conclusion just stated, we shall have to investigate first the length of each period, in other words, determine how many elements intervene in the table, according to increasing atomic weight between two with analogous properties.

It has already been shown that for the elements as far as chlorine, a period always includes seven elements. After chlorine comes potassium (39), which thus falls into the column under sodium. The following elements,

K 39.1   Ca 40   Sc 44.1   Ti 48.1   V 51.2   Cr 52.1   Mn 55.0

correspond very well with the preceding series,

Na 23   Mg 24.4   Al 27.1   Si 28.4   P 31.0   S 32   Cl 35.5

at least so far as the valence and the form of the compound are concerned ( $\text{Al}_2\text{O}_3$  and  $\text{Sc}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{SiO}_2$ ,  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{SO}_4$ ,  $\text{KMnO}_4$  and  $\text{KClO}_4$ ), although the similarity of these elements in other respects is not very marked.

The elements following manganese, viz., Fe 56, Co 59, Ni 58.7, however, do not fit in at all under K, Ca, Sc; but if we pass these by there follows another series of seven elements, which corresponds to the one beginning with potassium:

Cu 63.6   Zn 65.4   Ga 70   Ge 72   As 75   Se 79.1   Br 80

We therefore reach the conclusion that, after the first two periods of seven elements ending with chlorine must come one of seventeen elements (two of seven each, and three elements placed at the side), if the elements in the same vertical column are to correspond in their properties.

This *large period* of seventeen elements can, therefore, be added to the preceding *small period* of seven elements in the following way:

SMALL PERIOD.

Na23 Mg24.4 Al27.1 Si28.4 P31 S32 Cl35.5

LARGE PERIOD.

K39 Ca40 Sc44.1 Ti48.1 V51.2 Cr52.1 Mn55.0 Fe56.0 Co59.0 Ni58.7  
Cu63.6 Zn65.4 Ga70 Ge72 As75 Se79.1 Br80

In order to arrange in periods the elements whose atomic weights exceed eighty, it is again necessary to assume large periods, and, moreover, to leave several places vacant. In this manner we arrive at the scheme known as MENDELÉEFF'S table (see p. 284).

212. Group VIII, as has been said, owes its origin to the setting at the side of the elements included in it, for by this means the corresponding elements of groups I-VII could be brought under each other. It will thus be of importance to the system, if the nine elements of this group display so much analogy to each other that the grouping of them together appears actually justified. Now this is really the case, as is seen from the following study of their properties:

1. All these elements are of a gray color and difficultly fusible; indeed, osmium is one of the hardest of all metals to fuse (2500°); iridium melts at 1950°, wrought iron at 1500°, etc. The melting-point of iron is higher than that of cobalt, and the latter higher than that of nickel. A similar fall of this constant is found with ruthenium, rhodium and palladium, and also with osmium, iridium and platinum.

2. Their atomic volumes are small in comparison with the neighboring elements. The atomic volume of molybdenum is 11.2, that of ruthenium, rhodium and palladium about 9; that of silver 10.3; that of cadmium 13.0.

3. They display in marked degree the ability to let hydrogen pass through when red hot, or to condense it in themselves at ordinary temperatures. The former property is especially developed in iron and platinum, the latter in palladium.

4. It is only with these metals that we find  $RO_4$  compounds, in other words, they are the only ones which can be octivalent. The compounds  $OsO_4$  and  $RuO_4$ , for example, are known, and also those.



with carbon monoxide, as  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ . In general, we find here the ability to form compounds with carbon monoxide, e.g.  $\text{PtCl}_2 \cdot 3\text{CO}$ . In this last compound platinum can also be considered octivalent.

5. They form stable and, in most cases, very nicely crystallizing double-salts with potassium cyanide. Iron, ruthenium and osmium give compounds of the type  $\text{K}_4\text{RCy}_6$ ; cobalt, rhodium and iridium form  $\text{K}_3\text{RCy}_6$ , while the elements of the last column, nickel, palladium and platinum, give  $\text{K}_2\text{RCy}_4$  double-salts.

6. They all form colored salts: those of cobalt are red or blue; the nickel salts are green; all the rest are various shades of brown.

7. They all possess the ability to condense on themselves other gases than hydrogen in larger or smaller amounts; especially is this true of the platinum metals. Platinum and palladium absorb carbon monoxide greedily.

**213.** Let us now examine the seven other groups (vertical columns) more closely. If we bear in mind what was stated with reference to the large periods, it is clear that not all the elements in such a group display perfect chemical analogy. This is, however, the case when we compare with each other only those elements that belong to the even or the odd rows of the large periods. The similarity of the elements of these divisions is seen, in the case of the large periods, from the following facts:

1. Only the elements of the odd rows give hydrogen or alkyl compounds.

2. In the even rows the basic properties of the hydroxides are prominent, in the odd rows the acidic.

In general it may be said that, passing from left to right in the table, we meet first those that form the strongest bases and then gradually those that give acids. The latter property is most developed in the halogens, since they even form strong acids on combination with hydrogen.

A similar change is observed in going from the top to the bottom of the system. As the atomic weight increases the metallic (base-forming) nature of the elements in each group becomes more marked.

**214.** The periodic system of the elements is of value in four different directions:

1. In constructing a system of the elements.
2. In ascertaining the atomic weights of elements whose equivalent weights only could be determined.
3. In foretelling the properties of elements as yet undiscovered.
4. In confirming or correcting atomic weights.

Let us look at these various applications a little in detail :

### The Use of the Periodic Law in Constructing a System of the Elements.

215. After a careful comparison of the elements MENDELÉEFF reached the following important conclusion: *The entire character of an element, as displayed in its physical as well as in its chemical properties, is determined by the position which it occupies in the system and particularly by the four adjacent elements, the atomic analogues.* If an element is in an even series, the elements in the adjoining even series are its atomic analogues ; the same is true of the odd rows. From this it follows that, when the properties of an element are exactly known, its place in the system can be assigned. A couple of illustrations will make this clear.

The element beryllium possesses marked analogy to aluminium on the one hand and magnesium on the other; therefore it was a much discussed question whether its oxide should be given the formula  $\text{BeO}$  or  $\text{Be}_2\text{O}_3$ . Since, according to analysis, 9.4 parts Be combine with 16 parts O, the atomic weight would be in the former case 9.4, in the latter  $\frac{3}{2} \times 9.4 = 14.1$ . With the atomic weight 14.1 the element would stand between nitrogen and oxygen; as nitrogen and the elements of the sulphur group as well yield only acid-forming oxides, beryllium oxide would have to be an acid anhydride too, which is not the case, it being a basic oxide. Thus beryllium would not fit in the system with that atomic weight. If, however, it has the atomic weight 9.4, it falls in the horizontal series between the strongly basic lithium and the weakly acidic boron and over magnesium, with which it shows real analogy. This is indeed its fit place, i.e. its properties are those which must belong to an element in this position (see table). Farther, the properties of beryllium are to those of lithium as the properties of boron are to those of beryllium, or, in the form of a proportion:  $\text{Be} : \text{Li} :: \text{B} : \text{Be}$ . Just as lithium forms a more strongly basic oxide than beryllium, so the basic character of beryllium oxide is stronger than that of



boron oxide; again beryllium chloride is more volatile than lithium chloride, boron chloride more volatile than that of beryllium.

We also have the relation  $\text{Be} : \text{Mg} :: \text{Li} : \text{Na} :: \text{B} : \text{Al}$ , for beryllium oxide is less basic than magnesium oxide, lithium oxide than sodium oxide, boron oxide less than aluminium oxide. Beryllium fluoride dissolves in water, magnesium fluoride does not; similarly boron fluoride but not aluminium fluoride is soluble in water.

Finally we have  $\text{Be} : \text{Al} :: \text{Li} : \text{Mg} :: \text{B} : \text{Si}$ . The hydroxides of beryllium and aluminium are very similar to each other; they are gelatinous and soluble in alkalis. Both metals are scarcely acted upon by nitric acid and both dissolve in alkalis with the evolution of hydrogen. Their chlorides must be prepared in the same way from the oxides (by heating with charcoal in a current of chlorine). Likewise lithium and magnesium are analogous in certain respects; the carbonate and the phosphate of lithium, like the corresponding salts of magnesium, are very difficultly soluble, which is in marked contrast with the other metals of the lithium group. Boron and silicon both form very refractory oxides and salts; their fluorine compounds are decomposed by water in a similar manner, etc.

The evidence in accordance with which beryllium was assigned its present position in the system was subsequently confirmed directly by the determination of the vapor density of the chloride, which led to the formula  $\text{BeCl}_2$ . The vapor density of the beryllium compound of an organic substance (acetylacetone) also led to 9.4 as the atomic weight of beryllium.

As a second example let us take thallium. This element displays analogy with the alkali metals and also with aluminium, as well as with lead and mercury. According to its atomic weight it must lie between the two latter and belongs in the aluminium group. This position is justified when the following relation is taken into consideration:



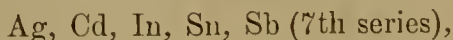
The highest stages of oxidation show unmistakable analogy, since the oxides have the same properties by pairs. The oxides of aluminium and thallium are weakly basic, those of mercury (ic) and magnesium more strongly, while lead dioxide and silica are weakly acidic. Thallium, mercury and lead all three form lower oxides of strongly basic character ( $\text{Tl}_2\text{O}$ ,  $\text{Hg}_2\text{O}$ ,  $\text{PbO}$ ), which aluminium, magnesium and silicon are unable to do. The oxide  $\text{Tl}_2\text{O}$

is comparable with  $K_2O$  in its properties, the lead monoxide with calcium oxide ( $Tl : K :: Pb : Ca$ ); see the table. In regard to the physical properties, it should be observed that in the matter of volatility thallium lies between mercury and lead.

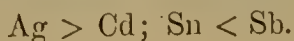
**Use of the System in Ascertaining the Atomic Weights of Elements whose Equivalent Weights only are known.**

216. A good instance is that of the very rare element indium. When the periodic system was established only the equivalent weight of indium was known, the analysis of the chloride having shown it to be 38, i.e. it was known that 38 parts of indium combine with 35.5 parts of chlorine. If this were the atomic weight and consequently  $In_2O$  the formula of the oxide, the element would have to occupy the place which potassium now has. Not only is this place taken but the oxide is only weakly basic, while it should have strongly basic properties if it belonged to the first group. If the atomic weight were 76, corresponding to the oxide  $InO$ , the element would stand between arsenic and selenium in the table; its oxide could not then have the formula  $InO$ , but would have to be  $In_2O_5$  or  $In_2O_3$  and have acid properties. On the other hand, there is no place for a metal with the atomic weight 76 and an oxide  $InO$  in the second group, where the oxides have this type. If the oxide be  $In_2O_3$ , the atomic weight of indium must be 114. Now, as a matter of fact, there is a vacant place in the system between  $Cd = 112$  and  $Sn = 119$  for an element with an  $R_2O_3$  oxide. In the same way as we have shown it for the oxides  $R_2O$  and  $RO$ , it can also be demonstrated that indium could not be located in the table with an oxide  $InO_2$ ,  $In_2O_5$ ,  $InO_3$ , etc. There remains, thus, no other possibility than to give the oxide the formula  $In_2O_3$  and the element an atomic weight of 114.

Let us now see whether the properties of the element and its compounds conform to this location. Two of its atomic analogues for this position are cadmium and tin. The oxides of both are easily reduced; this is true also of indium oxide. If, now, we consider the metals:



we notice first that the melting-point of silver lies higher than that of cadmium; likewise antimony melts higher than tin:



If indium fits in this series, it must, therefore, have the lowest melting-point of these five metals. This is actually the case; its melting-point is  $176^{\circ}$ . In the color of the metals there is a farther analogy; silver, cadmium and tin are white, and so is indium. As to the specific gravity: cadmium has the specific gravity 8.6, silver 10.5; the difference is thus 1.9. The difference of the specific gravities of tin and antimony is, on the contrary, small,  $7.3 - 6.7 = 0.6$ . If indium stands between these two pairs of elements its specific gravity should be smaller than the mean between cadmium and tin, i.e.  $\frac{1}{2}(8.6 + 7.3) = 7.9$ . In reality its specific gravity is 7.42.

The position of the metal requires that its oxide be feebly basic, weaker even than the oxides of cadmium and thallium ( $Tl_2O_3$ ), since cadmium is at the left and thallium farther down in the system (§ 215); on the other hand, it must be more strongly basic than the oxides of aluminium and tin. This condition also is fulfilled, as the following sets forth: the oxides of aluminium and tin, because of their slightly acid nature, dissolve in alkalis, forming definite compounds with the latter. The oxides of cadmium and thallium, however, are insoluble in alkalis; they are distinctly basic. Indium sesquioxide is soluble in alkalis, but forms no definite compound with them.

Finally, there is also the conduct of indium salts toward hydrogen sulphide which supports the placing of the element between cadmium and tin, for indium also is precipitated by hydrogen sulphide from acid solutions.

### Prediction of the Properties of Elements yet Undiscovered.

217. When MENDELÉEFF constructed his table, the elements gallium and germanium (fifth series) were still unknown. From the properties of the atomic analogues he ventured however at that time to predict the properties of these elements; thirteen years later WINKLER discovered an element with the atomic weight 72 (MENDELÉEFF had termed such an one "ekasilicon"; the discoverer named it *germanium*). Indeed there proved to be a very close agreement between the real properties and those predicted, as the following summary evidences:

Properties of ekasilicon predicted by MENDELÉEFF.	Properties of germanium discovered by WINKLER.
<ol style="list-style-type: none"> <li>1. The atomic weight must be the mean of the four atomic analogues Si, Sn, Zn, Se, i.e. <math>\frac{1}{4}(28.4 + 118.5 + 65.4 + 79.1) = 72.85</math></li> <li>2. The specific gravity (deduced as for indium above) must be 5.5.</li> <li>3. The atomic volume must lie between those of silicon (13) and tin (16), but be only a trifle above 13.</li> <li>4. Since it belongs in an odd series, it must be able to form alkyl compounds. Judging from analogies, the boiling-point of <math>\text{Es}(\text{C}_2\text{H}_5)_4</math> must be <math>160^\circ</math>, its specific gravity 0.96.</li> <li>5. The acid properties of <math>\text{EsO}_2</math> must be stronger than those of <math>\text{SnO}_2</math>.</li> <li>6. The specific gravity of <math>\text{EsO}_2</math> is 4.7.</li> <li>7. Since the oxides of indium and arsenic are easily reduced, this must also be true of <math>\text{EsO}_2</math>.</li> <li>8. <math>\text{EsS}_2</math>, because of its analogy with <math>\text{SnS}_2</math>, will probably be soluble in <math>\text{NH}_4\text{SH}</math>.</li> <li>9. <math>\text{EsCl}_4</math> is liquid, boils below <math>100^\circ</math> (since the boiling-point of <math>\text{SiCl}_4</math> is <math>57^\circ</math> and that of <math>\text{SnCl}_4</math> <math>115^\circ</math>), and has a specific gravity of 1.9.</li> <li>10. <math>\text{K}_2\text{SnF}_6</math> being more readily soluble in water than <math>\text{K}_2\text{SiF}_6</math>, the solubility of <math>\text{K}_2\text{EsF}_6</math> must also be greater than that of <math>\text{K}_2\text{SiF}_6</math>.</li> </ol>	<ol style="list-style-type: none"> <li>1. At. wt. = 72.</li> <li>2. Sp. g. = 5.469 at <math>20^\circ</math>.</li> <li>3. At. vol. = 13.1.</li> <li>4. Alkyl compounds were obtained. <math>\text{Ge}(\text{C}_2\text{H}_5)_4</math> boils at <math>160^\circ</math> and its specific gravity is a little less than 1.</li> <li>5. <math>\text{GeO}_2</math> lacks entirely the basic properties which are found to a limited extent in <math>\text{SnO}_2</math>.</li> <li>6. The specific gravity of <math>\text{GeO}_2</math> is 4.703 at <math>18^\circ</math>.</li> <li>7. <math>\text{GeO}_2</math> is easily reduced to the metal by heating with carbon or in hydrogen.</li> <li>8. <math>\text{GeS}_2</math> dissolves readily in <math>\text{NH}_4\text{SH}</math>.</li> <li>9. <math>\text{GeCl}_4</math> is liquid, boils at <math>86^\circ</math>, and has a specific gravity of 1.887.</li> <li>10. <math>\text{K}_2\text{SiF}_6</math> is almost insoluble; <math>\text{K}_2\text{GeF}_6</math> dissolves in 34 parts of boiling water.</li> </ol>

### Use of the Periodic System in Correcting Atomic Weights.

218. In the group of the platinum metals the atomic weights were previously determined by BERZELIUS and FREMY to be as follows: Os = 199, Pt 198, Ir 197. In this order the metals named do not, however, fit into the system, for osmium should be the first of the three on account of its analogy with iron and ruthenium, i.e. it should have the smallest atomic weight of the three. On the other hand, platinum, which is more akin to palladium, ought to have the highest atomic weight. A painstaking investigation by SEUBERT showed that in reality osmium has the atomic weight 191, iridium 193.0, and platinum 194.8, which order is in harmony with the system.

**219. Graphic representation.**—The fact that an arrangement of the elements according to increasing atomic weight also makes the gradual change of the physical properties evident can be seen most clearly from a graphic representation (as proposed by LOTHAR MEYER) in which the atomic weights are the abscissas and the atomic volumes the ordinates (see Plate I at end of book).

The first thing we notice in the curve is the regular rise and fall of atomic volumes. At the beginning of each period the atomic volume is at a maximum; it reaches a minimum half way through the large period (at the elements of group VIII) and then increases again. In the descending portions are the easily fusible, on the ascending the brittle elements. On the ascending portions are farther the gaseous and the easily fusible elements, on the descending at the minima the difficultly and very difficultly fusible. On the descending portions at the minima are the electro-positive, on the descending the electro-negative elements. The periodicity of the elements thus becomes very manifest.

The calculation of atomic volume is not always entirely free from uncertainties, inasmuch as we are not sure whether the specific gravity on which it is based represents in each case comparable conditions of the elements. Thus the temperature and the state of matter with which the specific gravity is concerned evidently play a certain rôle here. However, these factors are unimportant in the great majority of elements. The dotted portions of the curve connect those elements for which this uncertainty is greatest.

**220.** The discovery of the periodic system once more thrust into the foreground of interest one of the oldest of questions, viz., that concerning the *unity of matter*.

The striking connection between all the properties of the elements and their atomic weights leads unavoidably to the assumption of a *primordial* or *ground substance*. As to the nature of this no evidence is at present obtainable. PROUT, in 1815, regarded hydrogen as such. He observed that the atomic weights (then accepted) of many elements, based on hydrogen as unity, are whole numbers. Later, very accurate atomic weight determinations, particularly those of STAS, which were undertaken with the intention to confirm this hypothesis, demonstrated with certainty, however, that it was untenable.

**221.** The periodic system of the elements is one of the most important discoveries in the field of inorganic chemistry; it can never lose its importance, though it is gradually becoming more evident that the system in its present form represents the relations of the elements to each other merely in an approximate way and is only a crude first attempt at a real system.

There are indeed serious objections to the periodic system, which are of such a nature that some people rather hastily declare it to be absolutely worthless. These objections concern, in the first place, the positions which certain elements occupy in the system, and which agree very poorly with their properties. This is the case, e.g., with gold and copper which, indeed, show some analogy with lithium and sodium in their *ous*-compounds, but otherwise differ decidedly from the latter. The same is true of the metals of the cerium group (Ce, La, Nd, Pr, etc.). It cannot be denied that their atomic weights have been selected somewhat arbitrarily from the various (rather unharmonious) results of the determinations recorded, in order to fit them into the system; and even then the analogy with the other elements of the same group is still feeble. If the reply be made that these elements are still too little known because of their rarity and the great expenditure of energy and pains required for their investigation, it must be protested that the same is also true of those better known, such as cerium, and that if these elements should disclose themselves as complexes of several (which is not improbable), it is very doubtful whether there would be a place in the system for elements with approximately those properties which we are at present acquainted with in lanthanum, neodymium and praseodymium.

A second objection concerns the inability to fit all elements into the system. This is particularly the case with tellurium. Its physical and chemical properties put it without doubt in the sulphur group, and here there is a space for it, if its atomic weight were only about 125, or at least smaller than that of iodine (126.85). When the periodic system was first published, the atomic weight 128 was ascribed to tellurium; MENDELÉEFF predicted that more exact determinations would reduce the latter to about 125. Thereupon BRAUNER really did find the number 125 from a new determination. In a subsequent more careful investigation he obtained 127, however, and this figure was confirmed by MASUMI CHIKASHIGÉ, who used Japanese material in his research, while BRAUNER worked with European tellurium. Very recently, however, an organic compound of tellurium (diphenyl telluride) has been obtained, apparently in a very pure state. Its carbon determination leads to an atomic weight of 126.4. Still later work by PELLINI and also by KÖTHNER points to the value 127.6.

As to the elements discovered in the atmosphere since 1894, viz., *helium* (at. wt. 4), *neon* (20), *argon* (40), *krypton* (81.6) and *xenon* (128), it is clear that they form a natural group, for their properties display great analogy (see § 110). Since they are not able to form compounds with other elements, they can be regarded as zero-valent. In that case their group could find a place after the eighth, or before the first, group (compare the table, page 284), thus forming a bridge, or transition, from the strongest electro-negative, to the strongest electropositive, elements. However, it must be noted that argon with an atomic weight of 40 precedes potassium with an atomic weight of 39. As may be seen from Plate I, their atomic volumes fit into LOTHAR MEYER'S curve very well.

## LITHIUM AND SODIUM.

## Lithium.

222. This metal is not found free in nature; in combination, however, it is very widely distributed, although always in small amounts. Many mineral waters contain it. It occurs chiefly in the silicate *lepidolite*, or *lithia-mica*, also as the phosphate in *triphyllite* and in company with aluminium, sodium, and fluorine in *amblygonite*. Finally, lithium is met with in the ashes of certain plants, such as tobacco, indicating that it is also contained in the soil. With the aid of the spectroscope it can be detected in very many minerals.

Lithium can be obtained from lepidolite by the following very simple process: The mineral is fused and then poured into cold water, whereupon it becomes very brittle and its silicates are brought into such a condition that they can be decomposed by hydrochloric acid. The finely powdered mass is boiled with hydrochloric acid and the metals Ca, Al, Mg, etc., precipitated by soda from the resulting solution (after filtering off the silica), lithium and the other alkali metals remaining in solution. By evaporation a salt mixture is obtained from which the lithium chloride can be isolated by extraction with alcohol, the insoluble chlorides of sodium and potassium remaining behind.

Metallic lithium is prepared by electrolysis of the fused chloride or a concentrated solution of this salt in pyridine. It is the lightest of all solid substances, its specific gravity being only 0.59, so that it floats on coal-oil. It is silvery white but tarnishes very rapidly in moist air. Melting-point  $180^{\circ}$ . When heated in the air it burns with an intense white light to the oxide; at ordinary temperatures it is not so readily oxidized as sodium and potassium. It decomposes water with the evolution of hydrogen; the heat generated is insufficient, however, to melt the metal.

**Lithium oxide**,  $\text{Li}_2\text{O}$ , and **hydroxide**,  $\text{LiOH}$ . The former is obtained by heating the nitrate strongly. It dissolves in water slowly, forming the hydroxide. The latter is a white, crystalline substance, similar to caustic soda; it dissolves in water, producing a strongly alkaline solution.

**Lithium chloride**,  $\text{LiCl}$ , crystallizes anhydrous in regular octahedra; below  $0^{\circ}$  it takes up 2 mols. water of crystallization however. It dissolves very easily in water and deliquesces in moist air.

**Lithium carbonate**,  $\text{Li}_2\text{CO}_3$ , unlike the carbonates of the other alkalis, is difficultly soluble in water (100 parts of water at  $13^{\circ}$  take up 0.769 part); hence it can be precipitated from the concentrated solution of the chloride by ammonium carbonate.

**Lithium phosphate**,  $\text{Li}_3\text{PO}_4$ , is likewise very sparingly soluble in water (1 part in 2539 parts of water), although the phosphates of the other alka-

lies are readily soluble. The formation of this salt serves as a test for lithium.

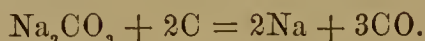
The *lithium spectrum* consists of two red bands, one of which in particular is easy to recognize.

### Sodium.

**223.** Sodium occurs in nature in enormous quantities and is very widely diffused. It is a constituent of countless silicates and, as a result of rock decay, gets into the soil, whence it enters the plants and finally reaches the animal organism. The nitrate is known as *Chili saltpetre*, the chloride as *rock salt*, or *halite*, the carbonate as *soda*; the *cryolite* (ice-stone) of Greenland is a sodium aluminium fluoride. Common salt, NaCl, constitutes the main part of the saline matter in sea-water. Certain bodies of water, such as the Dead Sea of Palestine and the Great Salt Lake in North America, are almost saturated solutions of common salt.

The metal was first obtained by DAVY in 1807 by the electrolysis of molten sodium hydrate. GAY LUSSAC and THÉNARD got it by heating sodium hydrate with powdered iron to white heat. The first named method is the one now generally employed for its commercial manufacture, inasmuch as electric power can be obtained quite cheaply. The metal is also prepared on a large scale by the electrolysis of fused sodium chloride.

The older commercial process was to heat a mixture of soda and coal dust at a high temperature:



This is carried out in iron retorts. The metal is vaporized and is condensed in shallow flat iron receivers under coal oil. It is then purified by fusing it under boiling coal oil of high boiling-point and pressing through linen sacks. Finally it is cast into plates, which are broken up, or into sticks, when it is ready for the market.

Sodium is silvery white, melts at  $95.6^\circ$  and boils at  $900^\circ$ , turning at the latter temperature to a colorless vapor. At ordinary temperatures it is very soft, so that it can be readily cut with a knife. It can also be easily pressed through a small hole, coming out in the form of wire. Sp. g. at  $13.5^\circ = 0.9735$ .

The molecule of sodium contains only one atom, as is proved



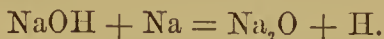
by the depression of the freezing-point of its solution in tin. A great many metals have this same property.

In moist air the bright surface of a freshly cut piece tarnishes rapidly, but in air that has been dried with phosphorus pentoxide it keeps its metallic lustre for days. Sodium can be heated in the air to melting and even still higher without catching fire. It ignites only when heated strongly, whereupon it burns with a very bright yellow light (especially in an atmosphere of oxygen). With water it generates hydrogen, sodium hydroxide being also formed. If it is held firmly in one place during this process (e.g. by laying it on a piece of filter paper floating on water, or upon ice), the hydrogen takes fire because of the localization of the heat production.

Sodium finds extensive use in the laboratory and in the arts. Because of its strong reducing-power it is often used to separate the elements from their oxides; magnesium and aluminium were formerly obtained thus. In organic chemistry it is also frequently employed for various purposes.

#### OXIDES AND HYDROXIDES OF SODIUM.

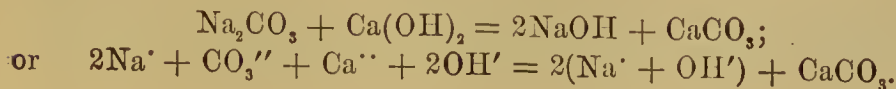
224. On burning sodium in dry oxygen a mixture of two oxides,  $\text{Na}_2\text{O}$  and  $\text{Na}_2\text{O}_2$ , results. The former is also obtained by heating sodium with caustic soda:



The product is a gray mass, which dissolves in water forming sodium hydroxide,  $\text{NaOH}$ , and giving off much heat.

The peroxide,  $\text{Na}_2\text{O}_2$ , is obtained by heating sodium in a current of oxygen till no more oxygen is absorbed. With 8 mols. water it forms a hydrate,  $\text{Na}_2\text{O}_2 + 8\text{H}_2\text{O}$ . Since it yields hydrogen peroxide with dilute acids and is a vigorous oxidizing agent it is manufactured commercially.

Sodium hydroxide,  $\text{NaOH}$ , *caustic soda*, is formed, together with metallic sodium, when sodium monoxide is reduced in a current of hydrogen. The ordinary method of preparing caustic soda consists in boiling soda with slaked lime:



As the solubility product (§ 73) of  $\text{CaCO}_3$  is very small, the ions  $\text{Ca}^{++}$  and  $\text{CO}_3^{--}$  must unite and the carbonate of lime sinks to the bottom. In order to make the decomposition of  $\text{Na}_2\text{CO}_3$  quite complete, a slight excess of slaked lime is added. Nevertheless, the solution does not contain an appreciable quantity of  $\text{Ca}(\text{OH})_2$ . The reason of this is clear: in the solution there are a large number of  $\text{OH}^-$ -ions; as a result the number of  $\text{Ca}^{++}$ -ions can only be very small, for the value of the solubility product of  $\text{Ca}(\text{OH})_2$  is reached with even a very weak concentration of the latter ions. The hydroxide is obtained by evaporation, whereupon it is often cast into sticks for the market. It is radiate-crystalline and very hygroscopic. It dissolves in water with the evolution of considerable heat. Sodium hydroxide is a very strong base; it is used in the arts for numerous purposes, among others the manufacture of soap.

#### SALTS OF SODIUM.

**225.** The sodium salts are of great industrial importance; many of them are prepared in enormous quantities. The starting-point for their manufacture is usually common salt.

**Sodium chloride**,  $\text{NaCl}$ , *common salt*, is found in large masses as rock-salt, e.g. at Stassfurt and Reichenhall and in Galieia, where it is dug out by miners. Farther, large amounts are obtained from sea-water and the water of salt-wells. Three methods are employed to remove the salt. In warm countries (e.g. on the coast of the Mediterranean) the water is let into flat basins of very large surface area ("salterns.") In these the water evaporates by the sun's heat and almost pure sodium chloride crystallizes out. Later on, the other salts of sea-water separate out; these are also worked up commercially. In countries with a cold climate (e.g. on the shores of the White Sea) the water is allowed to freeze in flat basins. The ice that forms is free from salt so that the remaining liquid is more concentrated.

In countries of the temperate zone the sea-water is concentrated by letting it evaporate spontaneously from a very large surface. This is done by the "graduation" process (Fig. 62). Bundles of fagots are piled up together in a "rick," above which a trough with small outlet-holes runs from end to end. The brine is pumped up into the trough and trickles down from along the entire length of the latter upon the brush; in this way the surface of the salt-

solution is greatly enlarged and the evaporation is made much more rapid. A very concentrated brine flows out at the bottom.

The salt is obtained from this concentrated solution by boiling ("salt-boiling.") Common salt is almost equally soluble in hot and cold water, hence it does not crystallize out on cooling but falls out at the same rate as the saturated brine evaporates, even while boiling hot. The salt obtained from the first crystallization is of course impure, containing small amounts of magnesium salts,

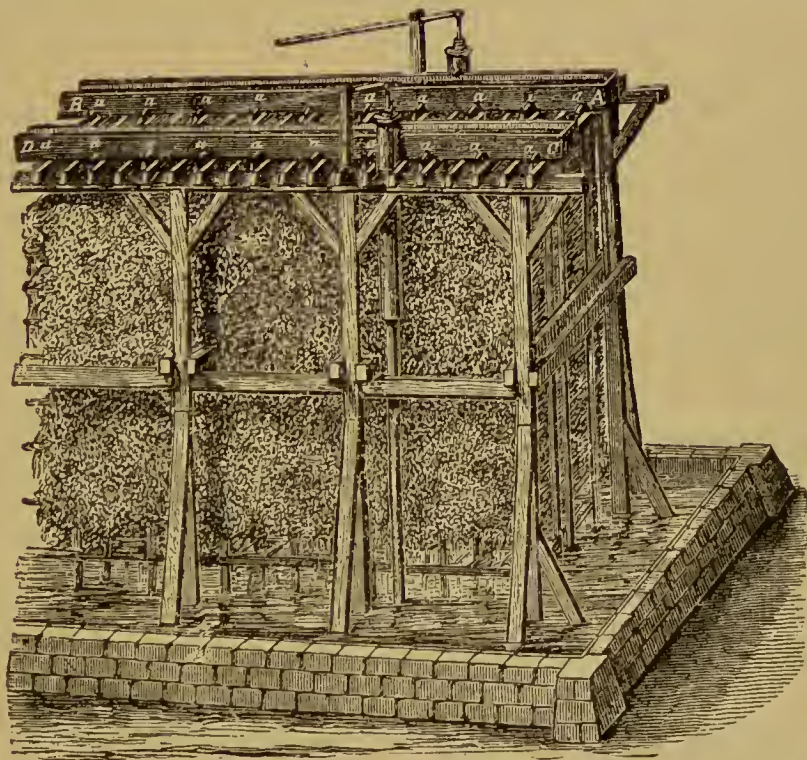


FIG. 62.—GRADUATION PROCESS.

which render it hygroscopic. In order to purify it, it is redissolved in water and again precipitated by evaporation.

Chemically pure sodium chloride is obtained by passing hydrochloric acid gas into a saturated solution of the salt or treating the solution with the concentrated acid. The sodium chloride is deposited because it is less soluble in hydrochloric acid than in water (§ 205).

Common salt crystallizes in cubes; when the solution evaporates slowly the well-known hollow four-sided pyramids or hopper-

crystals (Fig. 63) are formed. Sp. g. = 2.16. M.-pt. = 776°. 100 parts of water dissolve 36 parts NaCl at 0°, 39 parts at 100°; a saturated solution contains about 26% of salt. The crystals frequently enclose some of the mother-liquor; for this reason they decrepitate on heating. On cooling below -10° a saturated solution deposits crystals of the composition NaCl + H<sub>2</sub>O, which lose their water at 0°. Chemically pure sodium chloride is not hygroscopic. It is insoluble in absolute alcohol.



FIG. 63. — HOPPER-CRYSTAL OF SALT.

Sodium bromide, NaBr, and sodium iodide, NaI, are more soluble in water than the chloride. From hot solutions they crystallize in anhydrous cubes, below 30° in monoclinic crystals with 2 mols. H<sub>2</sub>O. NaBr is difficultly soluble, NaI easily soluble, in alcohol.

Sodium thiosulphate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> + 5H<sub>2</sub>O, is employed in photography (§ 247), in titrating iodine (§ 93) and as an antichlor (§ 82). It melts in its water of crystallization at 45° and forms super-saturated solutions very easily.

Sodium sulphate, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O (*sal mirabile Glauberi*, GLAUBER'S salt—so called after the discoverer) can be obtained in various ways: (1) by heating common salt with concentrated sulphuric acid; (2) by conducting a mixture of air, sulphur dioxide, and steam over hot sodium chloride (HARGREAVES' method):



(3) by the double decomposition of magnesium sulphate and sodium chloride at a low temperature (winter-temperature):



This last process is carried out at Stassfurt, where large masses of magnesium sulphate occur.

At ordinary temperatures Glauber's salt crystallizes with ten molecules of water; above 33° it goes over into a mixture of water and anhydrous salt; below 33° the hydrous salt, Na<sub>2</sub>SO<sub>4</sub>·10 aq, is again formed. The system Na<sub>2</sub>SO<sub>4</sub>·10 aq  $\rightleftharpoons$  Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O thus has a transition-point at 33°. This is confirmed by the fact that

the solubility of Glauber's salt in water suddenly changes at  $33^{\circ}$  from a rapid increase with rising temperature to a slow decrease.

This salt, like the preceding, forms supersaturated solutions easily. The solution saturated at  $33^{\circ}$  can be cooled down to room-temperature without any deposition if care is taken to exclude even the tiniest crystal of the salt (see § 237).

It is found that a perfectly sound crystal of  $\text{Na}_2\text{SO}_4 \cdot 10 \text{ aq}$  does not weather, but that when weathering has begun at any point it spreads over the crystal. The phase rule gives a satisfactory explanation of this phenomenon. We have in the Glauber's salt two substances,  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ ; in the case of a wholly unweathered crystal exposed to the air we have only two phases,  $\text{Na}_2\text{SO}_4 \cdot 10 \text{ aq}$  and  $\text{H}_2\text{O}$  (moisture of the air). According to the equation  $P + F = B + 2$  (§ 71) we still have in this system two degrees of freedom, i. e., the pressure of the water vapor and the temperature can both be selected arbitrarily (within certain limits). If, however, some weathered salt is present, the number of phases is three; then there is only one degree of freedom, or, in other words, every temperature has only one corresponding pressure and inversely every pressure only one temperature.

Glauber's salt is used in medicine; in the arts it is employed chiefly in the manufacture of soda.

**Sodium nitrate**,  $\text{NaNO}_3$ , called *Chili saltpetre* because of its extensive occurrence in Chili, crystallizes in rhombohedrons and melts at  $318^{\circ}$ . It is somewhat hygroscopic. Large quantities of it are used for fertilizing and also in the preparation of nitric acid and potash saltpetre.

**Sodium nitrite**,  $\text{NaNO}_2$ , is obtained by heating the nitrate, the addition of a reducing-agent such as lead or iron aiding the process. It is very soluble in water and is consumed in large quantities in the aniline-dye industry.

**Sodium phosphates.** Trisodium phosphate,  $\text{Na}_3\text{PO}_4 + 12\text{H}_2\text{O}$ , is split up in aqueous solution chiefly into sodium hydroxide and the secondary salt, for the solution reacts strongly alkaline and absorbs carbonic acid from the air. The ordinary "sodium phosphate" is the disodium phosphate,  $\text{Na}_2\text{HPO}_4$ , which separates from its aqueous solution at ordinary temperatures with twelve molecules of water in large crystals, that soon weather. 100 parts  $\text{H}_2\text{O}$  dissolve 9.3 parts of the salt at  $20^{\circ}$  and 24.1 parts at

30°. The solution is feebly alkaline. By leading in carbonic acid gas a liquid of *amphoteric* reaction is obtained, which turns blue litmus red as well as red litmus blue. Monosodium phosphate,  $\text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$ , reacts acid. It is converted by heat into the metaphosphate.

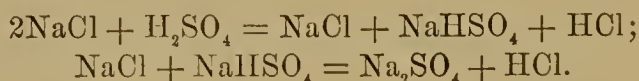
**226. Sodium carbonate**,  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$  (*soda, sal-soda*), is, next to the chloride, the most important sodium salt and it is manufactured on an enormous scale. It occurs in nature in Egypt, in America (Wyoming), on the Caspian Sea, and elsewhere; the ashes of many marine plants contain it.

The *manufacture of soda* is carried on by three different methods:

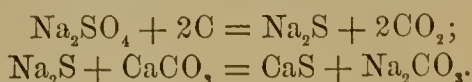
(1) The LE BLANC soda process.

This process was discovered by LE BLANC in 1794 and is still used to-day with no essential change. Formerly France imported most of its soda and potash. One of the first effects of the French Revolution was the cessation of this importation, so that the factories which consumed soda as their chief raw material suffered severely. Thereupon the French government urged chemists to devise methods of preparing soda from common salt. A commission was appointed to consider the plans submitted and preference was given to the method of the apothecary LE BLANC, who had already been conducting a soda factory after his method for some time. The discoverer was never able to enjoy the fruits of his great invention.

The LE BLANC process consists of three parts. In the first place common salt is warmed with strong sulphuric acid (chamber acid); hydrochloric acid and sodium sulphate (salt-cake) are formed:



In the second part of the process sodium sulphate is heated with coal and limestone, the following reactions taking place:



In case an excess of carbonate of lime is used the calcium sulphide, in the heating, goes over into a compound,  $\text{CaO} \cdot 2\text{CaS}$ , insoluble in water.

The third section of the process consists in lixiviating the mass (black-ash) last obtained with water, whereby sodium carbonate is dissolved out. The latter is then obtained from this solution by crystallization.

An important branch of the process is the utilization of the by-products. The hydrochloric acid is sold as such or else converted into chlorine (for the preparation of chloride of lime, etc.) From the insoluble residue ("tank-waste") the sulphur is recovered in different ways and converted anew into sulphuric acid.

The following is a more detailed account of the entire process.

*a.* The preparation of sodium sulphate, or the salt-cake process. Common salt and chamber acid are mixed in a large shallow iron pan *A* (Fig. 64) which is kept a trifle warm. Thus

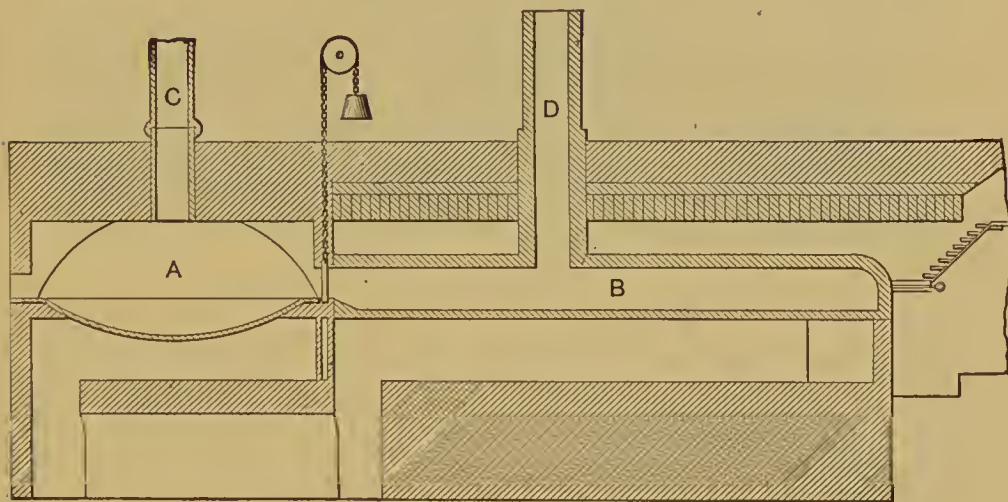


FIG. 64.—SULPHATE, OR SALT-CAKE, FURNACE

acid sulphate is formed while hydrochloric acid gas escapes in large amounts through *C*. This gas is conducted to the bottom of towers filled with coke and pieces of brick, over which water trickles and so becomes saturated with the ascending gas.

The reaction of the acid sulphate with sodium chloride to form Glauber's salt requires a higher temperature. Therefore, after the mixture of sulphuric acid and salt has been warmed in the pan for about an hour and has become solid, the sliding door is raised and the mixture raked over into a sort of muffle *B* which is heated directly over the open fire. The hydrochloric acid escapes through *D* and is again conducted through the absorption tower.

*b.* The formation of the soda, or black-ash process. The Glauber's salt is mixed with limestone, a little ignited lime and powdered coal (carbon), e.g. 10 parts of the salt, 7 parts of limestone, 0.7 part of lime and 7.5 parts of coal. The mixture is put in a horizontal cylinder which can revolve on a wide hollow axle (Fig. 65). The furnace flame passes through the axle. By turning the cylinder, a thorough mixing and even heating is brought about. After about two hours the reaction is ended and the black

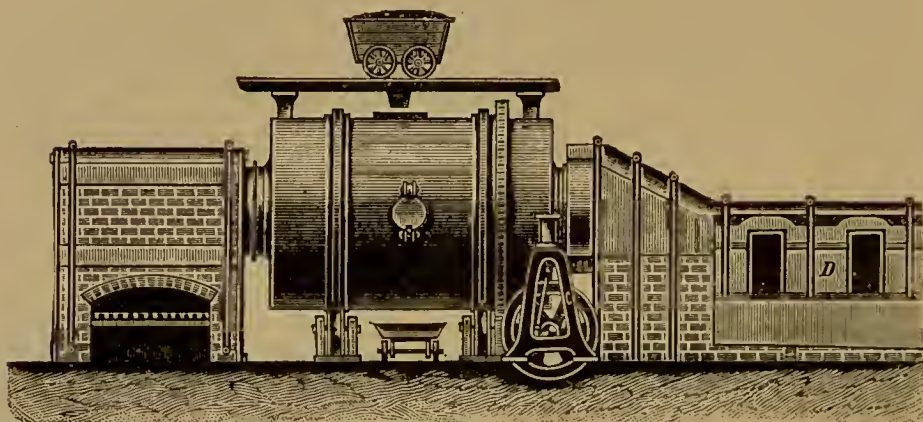


FIG. 65.—REVOLVING BLACK-ASH FURNACE.

molten mass is allowed to flow out by a door in the wall of the cylinder and down into small cars. The black color of the substance is due to the excess of coal employed. It contains calcium sulphide, lime and sodium carbonate, besides many other compounds in smaller amounts.

*c.* The extraction of the soda, or lixiviation of the ash. In this it is important to extract as large a quantity of the ash as possible with the least amount of water. This is accomplished by letting the water course through a series of tanks containing the pulverized ash. This is so conducted that the fresh water first reaches the vessel from which the soda is almost all extracted and then goes to the remaining ones richer and richer in soda, till finally, almost saturated, it meets the fresh ash (Counter-current principle).

Since a large excess of carbonate of lime is used and part of this goes over into lime on heating, a considerable amount of caustic soda is incidentally obtained. By treating this with carbon



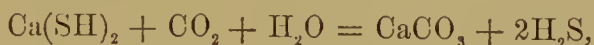
dioxide it is converted into soda. The entire solution is then evaporated in shallow tanks (at *D*, Fig. 65), the tanks being heated by the hot gases from the revolving cylinder. The resulting crystals are then calcined and yield crude soda.

The latter is farther purified by exposing it to a hot current of air. This oxidizes traces of sulphides to sulphates, also causing the yellow coloration due to the sulphides to disappear.

The soda residues, or tank-waste. This contains all the sulphur, which was used in the process in the form of sulphuric acid; the percentage of sulphur is 15–20%. It is therefore of very great importance to recover the sulphur from this waste and so be able to use it to make new sulphuric acid. This is done according to the method of CHANCE. The fresh waste is diluted with water to the consistency of a thin paste and then put into a system of high cylinders, through which the carboniferous gases from the lime-kiln are forced. The hydrogen sulphide, still very dilute, escaping from the first cylinder enters the second cylinder containing fresh waste and is there absorbed with the formation of calcium sulphhydrate:



At the same time the incidental constituents of the lime-kiln gases, such as nitrogen, escape. Finally the sulphuretted hydrogen is again expelled from the second cylinder by carbon dioxide:

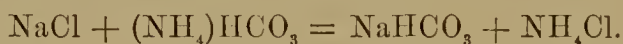


and is collected in large gasometers, the water of which is covered with a layer of petroleum. The gas so obtained contains about 33% of hydrogen sulphide. This is then burned to sulphur dioxide and the latter is converted into sulphuric acid in the lead chamber. In more modern plants the gas is at once burned as soon as it comes from the cylinders, although still mixed with carbon dioxide and nitrogen. The final residue in the cylinders consists chiefly of carbonate of lime with 2–3% of sodium carbonate. It can be used again in the soda process and is also quite desirable as raw material in the manufacture of cement. The hydrogen sulphide also yields sulphur by incomplete combustion; this sulphur is very pure. Part of the soda residues is, moreover, worked up into sodium thio-

sulphate; by slow oxidation of the former, calcium thiosulphate is formed, which can be extracted with water. Thereupon Glauber's salt is added, producing a double decomposition which precipitates calcium sulphate, while sodium thiosulphate stays in solution. The latter salt is obtained by evaporation.

(2) The ammonia-soda process of SOLVAY.

This process, which originally presented numerous technical difficulties, is now so perfected that it threatens to displace that of LE BLANC; in Germany already more than five-sixths of the total soda production is by the SOLVAY process. In England, however, the LE BLANC process is still most extensively used. The chemistry of the SOLVAY process is very simple. Ammonia and carbon dioxide are led alternately into a cold concentrated salt solution under pressure. The following reaction then takes place:



The acid sodium carbonate ("bicarbonate") so formed separates out, inasmuch as it is very difficultly soluble in the cold concentrated ammonium chloride solution. It is broken up by heating into soda and carbon dioxide, the latter of which is carried back to be used over. The ammonium chloride solution is distilled with lime or magnesia, whereby ammonia is recovered. The only waste-product, therefore, is chloride of calcium or chloride of magnesium, which can be worked up into hydrochloric acid or chlorine. Magnesium chloride, e.g., yields chlorine on heating in a current of air and is converted into magnesium oxide, which can be used anew in the decomposition of the ammonium chloride solution.

(3) Electrolytic Soda.

This process is based on the following actions: The electrolysis of an aqueous sodium chloride solution yields chlorine at the anode and at the cathode hydrogen and sodium hydroxide (see § 281). The anode is made of retort-graphite because it is indifferent to the action of nascent chlorine; the cathode is made of iron. By using mercury instead of iron, sodium amalgam is formed, from which the mercury can be recovered by distillation. The sodium hydroxide which is the product of this action is converted into the carbonate by passing in carbon dioxide.

The apparently very simple process of electrolysis of a sodium chloride solution, expressed ordinarily by the equations :



is in reality rather complicated. The resulting sodium hydrate is an electrolyte itself and is broken up into sodium and hydroxyl ions. The sodium immediately forms new hydrate of course, but without increasing the alkalinity, since it was previously present as caustic soda. The practical result is, therefore, a decomposition of water and there is a loss of electrical power proportional to the latter. Moreover the products of the electrolysis, sodium hydroxide and chlorine, interact forthwith, forming sodium hypochlorite. The hypochlorite diffuses in the solution and can be affected by the current in three ways: It can be split up by electrolysis, like every other salt of an oxy-acid, into base and acid, with the evolution of detonating gas; moreover it can be reduced at the cathode to sodium chloride; and, thirdly, it can be oxidized at the anode to sodium chlorate. The latter, however, can be itself electrolyzed or reduced.

Sodium carbonate crystallizes at ordinary temperatures with ten molecules of water of crystallization in large transparent monoclinic crystals, which soon turn white and dull from loss of water (weathering). They melt at  $60^\circ$  in their own water; on continued warming the hydrate  $\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$  is deposited; the latter loses 1 mol.  $\text{H}_2\text{O}$  in dry air and the remainder at  $100^\circ$ . At  $30^\circ$ – $50^\circ$  rhombic prisms of the composition  $\text{Na}_2\text{CO}_3 + 7\text{H}_2\text{O}$  crystallize out of the aqueous solution. 100 parts  $\text{H}_2\text{O}$  dissolve 6.97 parts of the anhydrous salt at  $0^\circ$ , 51.67 parts at  $38^\circ$ . The aqueous solution reacts strongly alkaline (§ 239).

Soda is used commercially on a large scale, particularly in the soap and glass industries. It is the "washing-soda" of the household.

**Acid sodium carbonate**,  $\text{NaHCO}_3$ , (bicarbonate of soda) is obtained as a primary product in the SOLVAY process. It dissolves in 10–11 parts of water at room-temperature and reacts alkaline. On being gently warmed it breaks up into carbon dioxide, water and soda; this decomposition occurs even on warming the aqueous solution, and when a current of air is passed through the concentrated solution at ordinary temperatures carbon dioxide escapes. It is used extensively in baking-powders and is the *saleratus* of commerce.

**Sodium silicate** (sodium water-glass) is prepared, among other ways, by fusing sand together with Glauber's salt and charcoal. It yields a vitreous mass, which is dissolved by boiling water. The concentrated solution has the consistency of glue. It finds use as a fixative in calico printing, farther for impregnating inflammable textiles like theater decorations, etc.; it is also used for "filling" soaps.

The **sulphides** of sodium correspond to those of potassium and are prepared in the same way (see Potassium).

**Sodium borate**: cf. Borax (§ 283).

## POTASSIUM.

**227.** Compounds of potassium occur in nature very extensively but not in such large quantities as those of sodium. Potassium exists principally in the silicates, especially feldspar and mica. Upon the decay of these it is carried into the soil and thence into the plants, to which potassium compounds are indispensable. In sea-water, also, potassium salts are found. The largest source of them is, however, the Stassfurt "*Abraum salts*" (§ 44), mainly double salts of potassium and magnesium, such as *carnallite*,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6 \text{aq}$ , *kainite*,  $\text{MgSO}_4 \cdot \text{KCl} + 3\text{H}_2\text{O}$ , etc.

The metal was first obtained by DAVY by the electrolysis of molten caustic potash. One of the commercial methods is to ignite a mixture of carbonate of potash and powdered charcoal (preferably charred potassium acid tartrate). The extraction of the metal is thus analogous to that of sodium; in the preparation of potassium, however, *potassium carbonyl* may be formed under certain circumstances, a substance which acquires explosive properties on exposure to the air.

Potassium has a silvery-white metallic lustre and is almost as soft as wax at ordinary temperatures. Sp. g. = 0.875 at 13°. It melts at 62.5° and boils at about 720°, forming a green vapor. The mirror-like surface of the metal immediately becomes dull in air; when heated in the air it burns with an intense violet light. Water is decomposed by it with great vigor, the heat evolved being sufficient to ignite the escaping hydrogen and to drive the piece of potassium around on the water.

### Oxygen Compounds of Potassium.

**228. Potassium oxide**,  $K_2O$ , is formed by the oxidation of thin shavings of potassium in dry air or by heating the peroxide with the metal. It is a white substance, which unites with water to form the hydroxide with the evolution of much heat.

**Potassium peroxide**,  $KO_2$ , is produced together with the monoxide on burning potassium in the air. It is dark yellow. In contact with water it yields potassium hydroxide, hydrogen peroxide and free oxygen.

**Potassium hydroxide**,  $KOH$ , results from the action of potassium on water and is generally prepared in the same manner as sodium hydroxide, viz., by treating potassium carbonate solution with milk of lime,  $Ca(OH)_2$ . Then, too, it is obtained by heating saltpetre with powdered copper (forming copper oxide and potassium oxide), and adding water; the copper oxide can be removed by filtration. The hydroxide usually comes on the market in sticks.

The commercial product ("caustic potash") is obtained chiefly by the first method and usually contains a little sulphate, chloride, etc., besides the carbonate which is gradually formed by the action of atmospheric carbon dioxide. It can be purified by treating with strong alcohol, which dissolves only the hydroxide; after filtering, the alcoholic solution is evaporated in a silver dish. Caustic soda is also purified in this way.

Potassium hydroxide is one of the strongest bases. In the solid state it greedily absorbs water and carbon dioxide from the air and finally deliquesces to a concentrated solution of potassium carbonate, while sodium hydroxide under these conditions turns to a solid white mass of soda. For this reason caustic potash is a much more suitable absorptive agent for carbon dioxide in analyses than caustic soda, for the use of the latter might easily cause a stopping up of the apparatus.

Caustic potash is used especially in the manufacture of soft soaps.

### Potassium Salts.

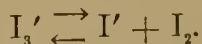
**229. Potassium chloride**,  $KCl$ , occurs at Stassfurt in the mineral *sylvite*. It crystallizes in cubes and melts at  $730^\circ$ . It is easily volatilized at elevated temperatures. 100 parts  $H_2O$  dissolve 25.5

parts KCl at 0°, 57 parts at 100°. Like its sodium analogue, potassium chloride is precipitated from its saturated solution by hydrochloric acid. It unites with many salts to form double salts.

**Potassium bromide**, KBr, is important therapeutically. It is prepared by mixing bromine with a potassium hydroxide solution, the bromide and the bromate being formed; the bromate is reduced by heating the salty product with powdered charcoal. Potassium bromide crystallizes in cubes and dissolves readily in water.

**Potassium iodide**, KI, also of medicinal value, can be prepared like the bromide and also in the following manner: Iodine and iron filings are placed together under water, whereupon a solution of the compound  $\text{Fe}_3\text{I}_8$  is formed; on treating this with a solution of potash the oxide  $\text{Fe}_3\text{O}_4$  is precipitated, carbon dioxide escapes and potassium iodide is left in solution; the salt is then obtained by filtration and evaporation. It crystallizes in cubes and is very soluble in water: 1 part  $\text{H}_2\text{O}$  dissolves 1.278 parts KI at 0°. On exposure to light or the air the crystals gradually turn yellow because of the separation of iodine.

It was remarked in § 46 that iodine, though only slightly soluble in water, dissolves considerably when the water contains potassium iodide. This is due to a compound which iodine forms in the latter case; it seems not improbable that such a solution contains  $\text{I}_3'$  ions. That iodine has entered into combination may be concluded from the fact that carbon disulphide takes up nearly all the iodine from an aqueous solution of the latter when it is shaken with the solution, but only a small proportion when the same operation is performed with a solution of iodine in a dilute aqueous solution of potassium iodide. Nevertheless, a solution of iodine and potassium iodide in water behaves in many cases as if all the iodine was present in the free state, e.g. when it is titrated with sodium thiosulphate. This must be explained by the supposition that in the liquid we have the equilibrium:



If the free iodine is now taken away, the equilibrium is disturbed, a new portion of  $\text{I}_3'$  must therefore split up, and so on till it has wholly disappeared.

**Potassium fluoride**, KF, possesses a peculiar property, which is lacking with the other halogen compounds of potassium: it com-

bines with hydrofluoric acid eagerly, forming the double halide  $\text{KF.HF}$ .

**Potassium cyanide**,  $\text{KCN}$  (often also written  $\text{KCy}$ ) is manufactured on a large scale by fusing yellow prussiate of potash with potash.



The cyanate of potassium  $\text{KCNO}$  is reduced by the iron to potassium cyanide also. It is very soluble in water, forming a strongly alkaline solution. On account of its great tendency to form double salts, it is employed in electro-metallurgy. It is also used in extracting gold from its ores (§ 248).

**Potassium chlorate**,  $\text{KClO}_3$ , can be obtained by passing chlorine into a hot solution of caustic potash (§ 56). It is now prepared almost exclusively by the electrolysis of a hot solution of potassium chloride; however, it is more advantageous to first prepare sodium chlorate in this way, and then treat this with potassium chloride, because sodium chlorate is much more soluble and does not retard the electrolytic process by separating from the solution, as does potassium chlorate.

Potassium chlorate is a well crystallized salt, which is used for the preparation of oxygen (§ 9); farther, it is used in the manufacture of matches and fireworks, and also medicinally as a remedy for sore throat. On being heated it gives up oxygen, part of the salt being at the same time converted into **potassium perchlorate**,  $\text{KClO}_4$ .

The last named salt is difficultly soluble in water. It is sometimes found in crude Chili saltpetre, rendering it unfit for use in fertilizing various cultivated plants.

**Potassium sulphate**,  $\text{K}_2\text{SO}_4$ , is obtained by the action of sulphuric acid on potassium chloride. It crystallizes in beautiful, lustrous rhombic prisms and dissolves with some difficulty in cold water (1 part in 10 parts  $\text{H}_2\text{O}$  at room-temperature). It is used principally for the preparation of potash according to the **LE BLANC** method. **Acid potassium sulphate**,  $\text{KHSO}_4$ , is very soluble in water; it melts at  $200^\circ$ , losing water and going over into **potassium pyrosulphate**,  $\text{K}_2\text{S}_2\text{O}_7$ . The latter breaks up into potassium sulphate and sulphur trioxide on heating.

**Potassium nitrate**,  $\text{KNO}_3$ , is widely distributed in nature,—although usually found only in small amounts,—for it is formed wherever nitrogenous organic bodies decay in contact with potassium compounds. This is the basis of an artificial method of preparing saltpetre, which method was formerly much used.

In the so-called *saltpetre plantations* manure, animal refuse, etc., are mixed with wood-ashes (containing potash) and lime and the mixture divided up into loosely packed heaps, which are frequently turned over so as to expose all parts to the air. A certain bacterium (*Bac. nitrificans*) conveys the oxygen of the air to the nitrogen compounds of the organic matter and oxidizes them to nitric acid, which forms nitrates with the bases present. After two or three years the heaps are lixiviated with water and potash is added to the solution, thus converting the calcium and magnesium nitrates into saltpetre, while calcium and magnesium carbonates are precipitated. Finally the saltpetre is purified by crystallization.

Another process of manufacture depends on the double decomposition of Chili saltpetre with potassium chloride, which is obtained in large quantities at Stassfurt:



For this purpose hot-saturated solutions of the two salts are brought together. As sodium chloride is much less soluble than saltpetre at the temperature of boiling water, it is the first to crystallize out on evaporation, but when the solution is cooled the saltpetre comes out first, for it is much less soluble than sodium chloride in cold water.

Potash saltpetre crystallizes without water in prisms, either rhombohedral or rhombic according to the temperature. In the neighborhood of the melting-point the former is the stable variety, at ordinary temperatures the latter. The location of the transition-point of the two forms has not yet been ascertained. 100 parts  $\text{H}_2\text{O}$  dissolve 13.3 parts  $\text{KNO}_3$  at  $0^\circ$ , 247 at  $100^\circ$ . It melts at  $338^\circ$ ; farther heating breaks it up into potassium nitrite and oxygen. It has a cooling taste.

**230.** Potash saltpetre is consumed in large quantities in the manufacture of *gunpowder*. This is a mixture of sulphur, charcoal and potash saltpetre, the proportions varying in different countries, but being in most cases 75%  $\text{KNO}_3$ , 10% S and 15% of charcoal.



These proportions of the three ingredients correspond very closely to 2 molecules  $\text{KNO}_3$ , 1 atom S, and 3 atoms C, which would call for 74.8%  $\text{KNO}_3$ , 11.8% S and 13.4% C. One might therefore be inclined to express the decomposition of gunpowder, in the main, by the equation :



The chemical reactions which come into play in the explosion of gunpowder are really much more complex, however. ABEL and NOBEL have investigated the products formed when it explodes under conditions analogous to those in firing a gun. They found that about 55–58% of solid matter remains, i.e., about 45–42% goes off as gas. The solids are at least half potash, while potassium sulphate and thiosulphate also are found in considerable quantities. The gases are chiefly carbon dioxide and nitrogen, and carbon monoxide in a smaller quantity. The tension of the gaseous products amounted to about 6400 atmospheres and the temperature attained was about 2200°.

The solid products of the combustion of gunpowder become very finely divided as a result of the explosion and remain suspended in the air for a long time as smoke. Gunpowder (black powder), which was formerly the only explosive material in use, is now being supplanted more and more by *smokeless* powder. This consists of organic substances which yield only gaseous products on exploding, and hence there is no smoke. (See HOLLEMAN'S *Organic Chemistry*.)

**231. Potassium phosphates.** The three potassium salts of phosphoric acid are known. They are very soluble in water

**Potassium carbonate**,  $\text{K}_2\text{CO}_3$ , *potash*. This salt was formerly obtained solely from wood-ashes, these being soaked in water and the strained liquor evaporated. At present it is manufactured extensively from potassium chloride after the LE BLANC process. Another source of potash is the molasses of the beet-sugar factories, that contains the potassium salts in which the sugar-beet is rich.

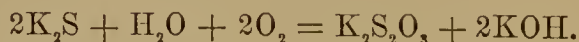
Potassium carbonate forms a white powder, which deliquesces in the air and is very soluble in water (1.12 parts  $\text{K}_2\text{CO}_3$  in 1 part  $\text{H}_2\text{O}$  at 20°); the solution has a strong alkaline reaction. The salt melts at 838°. It is used in the preparation of soft soaps and hard glass (potash-glass).

**Potassium silicate**, potassium water-glass, is formed when sand is fused with potash. Different salts of this sort are described. They dissolve in water, forming a thick, mucilaginous mass which on drying turns to a vitreous, and finally opaque, product. Potas-

sium water-glass is used for the same purposes as sodium water-glass.

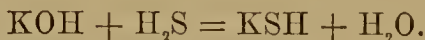
### Sulphides of Potassium.

**Potassium monosulphide**,  $K_2S$ , is prepared by reducing potassium sulphate with charcoal. It dissolves in water very readily and crystallizes out with five molecules of water. It absorbs oxygen from the air, going over into thiosulphate and potassium hydroxide:



Acids react with it, liberating hydrogen sulphide.

**Potassium hydrosulphide**,  $KSH$ , is obtained by saturating a caustic potash solution with hydrogen sulphide:



It is very soluble in water, the solution reacting alkaline; on evaporation *in vacuo* the solution deposits crystals of  $2KSH + H_2O$ . With potassium hydroxide it forms the monosulphide:



**Potassium polysulphides.** When a solution of potassium monosulphide is boiled with sulphur, we obtain the compounds  $K_2S_3$ ,  $K_2S_4$ ,  $K_2S_5$ . A mixture of these substances is also obtained by fusing potash with sulphur; besides these it contains the sulphate and the thiosulphate and is called *hepar sulphuris* ("liver of sulphur") because of its liver-brown color. These polysulphides are decomposed by acids with the evolution of hydrogen sulphide and the separation of sulphur:



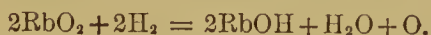
### Rubidium and Cæsium.

**232.** These elements are widely distributed, but always occur in extremely small amounts. The silicate *lepidolite*, or lithia mica, frequently contains a little rubidium. The exceedingly rare mineral *pollux* from the isle of Elba is a silicate of aluminium and cæsium, and contains about 30%

cæsium oxide. In general these elements are found wherever potassium salts are met with : in mineral springs, in the Stassfurt salts (e.g. carnallite contains rubidium), etc. They were discovered by BUNSEN and KIRCHHOFF in 1860 with the aid of spectrum analysis (§264); they obtained their names from the most important lines in their spectra (*rubidus* = dark red; *cæsius* = sky-blue).

In order to separate them from the large amount of potassium salts with which they generally occur, they are converted into chlorides and the solution is evaporated, whereupon the dry residue is extracted with strong alcohol. Almost all the sodium chloride and potassium chloride remains behind, while the chlorides of rubidium and cæsium dissolve. Platinum chloride is then added to precipitate  $K_2PtCl_6$ ,  $Rb_2PtCl_6$ , and  $Cs_2PtCl_6$ ; the solubility of these double salts in water is quite different (at 10° 100 parts  $H_2O$  dissolve 0.9 parts  $K_2$ -salt, 0.154  $Rb_2$ -salt, and 0.05  $Cs_2$ -salt), so that they can be very well separated by fractional extraction with boiling water. The rubidium iron "alum" is particularly well suited for the purification of rubidium salts, and especially for their separation from potassium salts, since it is readily soluble in hot, and only slightly soluble in cold water, and moreover crystallizes beautifully; potassium iron alum, on the other hand, is very soluble even in cold water.

The metals rubidium and cæsium are best obtained by heating their hydroxides with magnesium powder in an iron pipe. Rubidium has a silvery lustre, melts at 38.5, and has a specific gravity of 1.522 at 15°. The metal oxidizes very rapidly in the air or in oxygen, forming dark brown crystals of the peroxide,  $RbO_2$ . On being heated in a current of hydrogen it yields the hydroxide and free oxygen:



The hydroxide is a very strong base; its salts show much similarity to the analogous potassium compounds; they are in several instances less soluble, e.g. Rb-alum, Rb-perchlorate (§ 60), etc.

Cæsium is a silvery white metal; sp. g. 1.85; m. p. 26.5°; b. p. 270°. It soon takes fire on exposure to the air. The salts of cæsium are very similar to those of rubidium; some of them are even less soluble, and are therefore used for the preparation of pure cæsium compounds. This is particularly true of the platinum double salt already mentioned and the cæsium alum and the acid tartrate.

Rubidium bromide and iodide, but more so the corresponding compounds of cæsium, have the property of combining with two atoms of bromine or iodine, forming yellow or brown colored crystalline compounds; these metals can thus be trivalent.

## SUMMARY OF THE GROUP OF ALKALI METALS.

233. The gradual change of the physical properties of these metals with increasing atomic weight is made plain by the following table:

	Li	Na	K	Rb	Cs
Atomic weight...	7.03	23.05	39.15	85.4	133
Spec. gravity ...	0.59	0.97	0.865	1.52	2.4
Melting-point...	180.0°	97.6°	62.5°	38.5°	26°-27°
Boiling-point....	Red heat	742°	667°	.....	270°
Atomic volume .	11.8	23.7	45.3	56.7	55.3

The specific gravity increases with the atomic weight, as does also the atomic volume; on the other hand, there is a fall in the melting- and boiling-points.

From a chemical standpoint we notice, in the first place, the same general type in the compounds, showing that all these elements are univalent. The hydroxides all have the formula ROH, the halogen compounds RX, etc. The salts of them all, particularly even the carbonates and phosphates, are soluble in water (although in different degrees), the former with basic reaction. The metals all oxidize very readily in the air.

On the other hand, we cannot overlook the fact that the metals potassium, rubidium and caesium, which are very similar to each other, differ from sodium and lithium in many respects. The latter displays, as we shall see in the sequel, analogy with magnesium in several important points, thus differing from the metals of its own group. A slight divergence in the behavior of the first members of a group from that of the rest is found to characterize almost all of the groups. We may recall carbon, for instance, the first member of the fourth group, which differs distinctly from silicon and the rest in the ability of its atoms to unite with each other; also fluorine with its soluble silver compound; still other examples of this sort will be met with later.

Sodium differs from the sub-group, K, Rb, Cs, in the solubility of its salts. The sodium salts are almost all readily soluble in water; this is true even of the platinum double salt,  $\text{Na}_2\text{PtCl}_6$ , the acid

sodium tartrate and others. Soda crystals weather, while potash deliquesces in the air. The spectra of sodium, on the one hand, and the other alkali metals, on the other, are entirely dissimilar.

### Ammonium Salts.

**234.** In the description of ammonia (§ 111) it was already observed that it combines with acids directly, forming salts which are very similar to those of potassium, and in which the group,  $\text{NH}_4$ , the *ammonium* group, is assumed to exist. In connection with the alkali group a description of a few ammonium salts may find a place.

The aqueous solution of ammonia must, because of its electrical conductivity and its alkaline reaction, contain  $\text{NH}_4$  and  $\text{OH}$  ions and hence also undissociated molecules of ammonium hydroxide,  $\text{NH}_4\text{OH}$ . While solutions of the alkalies,  $\text{KOH}$ ,  $\text{NaOH}$ , etc., conduct the electric current very well, this is not the case with an ammonia solution; it is a poor conductor. A solution of 1 g.  $\text{NH}_3$  in 1 liter of water contains only one per cent of ionized  $\text{NH}_4\text{OH}$  molecules.

This is due to the fact that the solution contains chiefly  $\text{NH}_3$  molecules and only a little  $\text{NH}_4\text{OH}$  so that the concentration of the  $\text{NH}_4$  and  $\text{OH}$  ions is necessarily weak. Moreover, since the tension of the ammonia gas above the solution approximately obeys Henry's law, it is probable that the ammonia and the water are combined only to a small extent (cf. § 29).

The same conclusion is reached from the fact that solutions of the primary, secondary and tertiary amines (Organic Chemistry, § 70) also display a conductivity not much greater than that of ammonia itself, while the quaternary ammonium bases, on the contrary, are very good conductors. In the latter instance the molecule can no longer break up into  $\text{NR}_3$  ( $\text{R}$  = alkyl or hydrogen) and  $\text{H}_2\text{O}$ .

On account of the volatility of ammonia and the extensive dissociation of  $\text{NH}_4\text{OH}$  into  $\text{NH}_3$  and  $\text{H}_2\text{O}$  the ammonium salts are easily decomposed.

**Ammonium chloride**,  $\text{NH}_4\text{Cl}$ , *sal ammoniac*, is obtained from the ammonia liquor of the gas factories. The ammonia is expelled by warming and absorbed in hydrochloric acid; this solution is evaporated and the solid residue sublimed, whereby the salt is obtained in compact fibrous masses. It dissolves in 2.7 parts of cold, and in 1 part of boiling, water and crystallizes out of the solution in small,

usually feather-like groups of octahedrons or cubes. It has a sharp saline taste.

Ammonium chloride vaporizes easily, dissociating into ammonia and hydrochloric acid, as is shown by the vapor density, which at  $350^{\circ}$  is only half as great as calculated.

This dissociation can be easily demonstrated in the following manner: Introduce into a tube sealed at one end a little ammonium chloride and, not far from this, a piece of blue litmus paper. In front of the latter is pushed a cotton wad and finally a piece of red litmus paper. The chloride is then heated. Since hydrochloric acid has a smaller diffusion-velocity than ammonia the latter passes through the wad first and colors the red paper blue; as a result an excess of hydrochloric is left at the other end and it reddens the blue paper placed there.

It is a remarkable fact, discovered by BAKER, that perfectly dry ammonium chloride (having stood for a long time in a desiccator over resublimed phosphorus pentoxide) has the normal vapor density. On the other hand, the same investigator found that similarly dried ammonia gas and hydrochloric acid gas do not unite to form ammonium chloride (§ 38). Traces of water are thus seen to produce a marked catalytical acceleration, both of the formation and of the decomposition of ammonium chloride. We have here an illustration of the general rule that when one part of the system in a reversible reaction is accelerated by a catalyzer the other must be likewise affected. The proof of this rule lies in the impossibility of the contrary being true, since that would necessitate a change in the equilibrium (see § 49).

**Ammonium sulphate**  $(\text{NH}_4)_2\text{SO}_4$ , crystallizes in large rhombic prisms and dissolves very readily in water. On boiling the aqueous solution some ammonia escapes, acid sulphate being formed.

**Ammonium nitrate**,  $\text{NH}_4\text{NO}_3$ , deliquesces in the air; when heated it breaks up into water and nitrous oxide (§ 119). This salt is known in three crystallized modifications, the transition-points (§ 70) of which have been determined.

**Ammonium phosphates.** The tertiary salt,  $(\text{NH}_4)_3\text{PO}_4$ , is deposited in crystalline form on mixing concentrated solutions of phosphoric acid and ammonia. It cannot be dried, however, for it then loses ammonia and goes over into the secondary  $(\text{NH}_4)_2\text{HPO}_4$ . On boiling the solution the salt again yields ammonia and is transformed into the primary phosphate.

The best known salt of this kind is **sodium ammonium phosphate**,  $\text{NaNH}_4\text{HPO}_4 + 4\text{H}_2\text{O}$ , *microcosmic salt*. It forms large transparent crystals. On being heated it melts, loses water and ammonia, and passes over into a vitreous substance, sodium metaphosphate,  $\text{NaPO}_3$ .

**Ammonium carbonate** was formerly obtained by the dry distillation of nitrogenous organic substances, such as hair, nails, leather, etc., hence the name "salt of hartshorn," which still clings to it. At present, however, it is made by dry distilling a mixture of calcium carbonate and ammonium chloride or sulphate. The product is a mixture (molecule for molecule) of acid salt,  $\text{NH}_4\text{HCO}_3$ , and ammonium carbamate,  $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{NH}_4$  (this latter being the neutral salt minus  $1\text{H}_2\text{O}$ ). From its composition  $(\text{NH}_3)_3(\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ , it takes the name *ammonium sesquicarbonate*. On passing ammonia gas into a concentrated aqueous solution of it the neutral salt  $(\text{NH}_4)_2\text{CO}_3$ , separates out as a crystalline powder; it smells strongly of ammonia and passes slowly over into the acid salt,  $\text{NH}_4\text{HCO}_3$ , a white odorless powder, which is scarcely soluble in water. This acid salt is also formed directly from the sesquicarbonate, as the latter gives off carbon dioxide and ammonia in the air (hence the odor of ammonia) and goes over into the first-named salt.

**Ammonium sulphide** is extensively used in analysis (§ 73). A solution of ammonium hydrosulphide (or sulphhydrate),  $\text{NH}_4\text{SH}$ , is obtained by saturating aqueous ammonia with hydrogen sulphide; it is a colorless liquid, which soon turns yellow because of the formation of ammonium polysulphides. The oxygen of the air oxidizes part of the hydrogen sulphide and thus sets free sulphur, which combines with ammonium hydrosulphide to form polysulphides. These polysulphides are also obtained by dissolving sulphur in a solution of ammonium hydrosulphide.

On mixing 2 vols.  $\text{NH}_3$  gas and 1 vol.  $\text{H}_2\text{S}$  gas at  $-18^\circ$  a white crystalline mass is obtained, which decomposes at ordinary temperatures into  $\text{NH}_4\text{SH}$  and  $\text{NH}_3$ . The compound  $\text{NH}_4\text{SH}$  separates out crystalline when hydrogen sulphide is passed into alcoholic ammonia. As low as  $45^\circ$  it is completely dissociated into equal volumes of  $\text{NH}_3$  and  $\text{H}_2\text{S}$ .

## SALT SOLUTIONS.

235. Every solid substance is soluble in every liquid; however, the proportion which dissolves can vary all the way from zero to infinity. If only an infinitesimal amount of the solid goes into solution, we say ordinarily that the substance is "insoluble" in the liquid; there can be no doubt, however, that, if our means of investigation were sufficiently improved and large enough quantities of liquid employed, the solubility would be perceptible. In many cases of so-called insoluble substances this has been able to be demonstrated with certainty. Even when we confine our attention to aqueous solutions of salts (including acids and bases) we find the same infinite difference in solubility that is observed between substances in general. Substances such as sand, barium sulphate (§ 262), silver iodide, etc., are "insoluble"; others like sulphuric acid are able to dissolve in any given amount of water.

The solubility, i.e. the maximum amount of salt that can go into solution, is a function of the temperature and the pressure; as to the former, the solubility increases with the temperature in the great majority of cases. If the temperature is plotted on the axis of abscissas and the amount of salt which dissolves in one hundred parts of water is plotted on the ordinate axis, a solubility curve is obtained (Fig. 66) which makes plain the above statements.

With some salts, e.g. potassium nitrate, the solubility increases very rapidly with the temperature; for sodium chloride it remains practically constant. In certain cases, such as those of calcium hydroxide and gypsum (within certain limits of temperature) the solubility decreases with rising temperature. These phenomena are connected, as has already been explained, with the *heat of solution*, i.e. with the caloric effect which accompanies the process of solution, and in the manner expressed by VAN'T HOFF'S principle of mobile equilibrium (§ 103). In fact saltpetre, for instance, whose solubility increases very rapidly (see Fig. 66) with the temperature, dissolves in water with a considerable absorption of heat.

236. The term *heat of solution* has various meanings. We are obliged to distinguish between (1) the caloric effect of dissolving a salt in a very large amount of water; (2) the caloric effect of dissolving a salt in an almost saturated solution; and (3) the total heat of solution, i.e. the whole



caloric effect of dissolving a salt in water until the latter is saturated. As a rule these three magnitudes will have dissimilar values, indeed their algebraic signs may be opposite. This is the case, for instance, with the

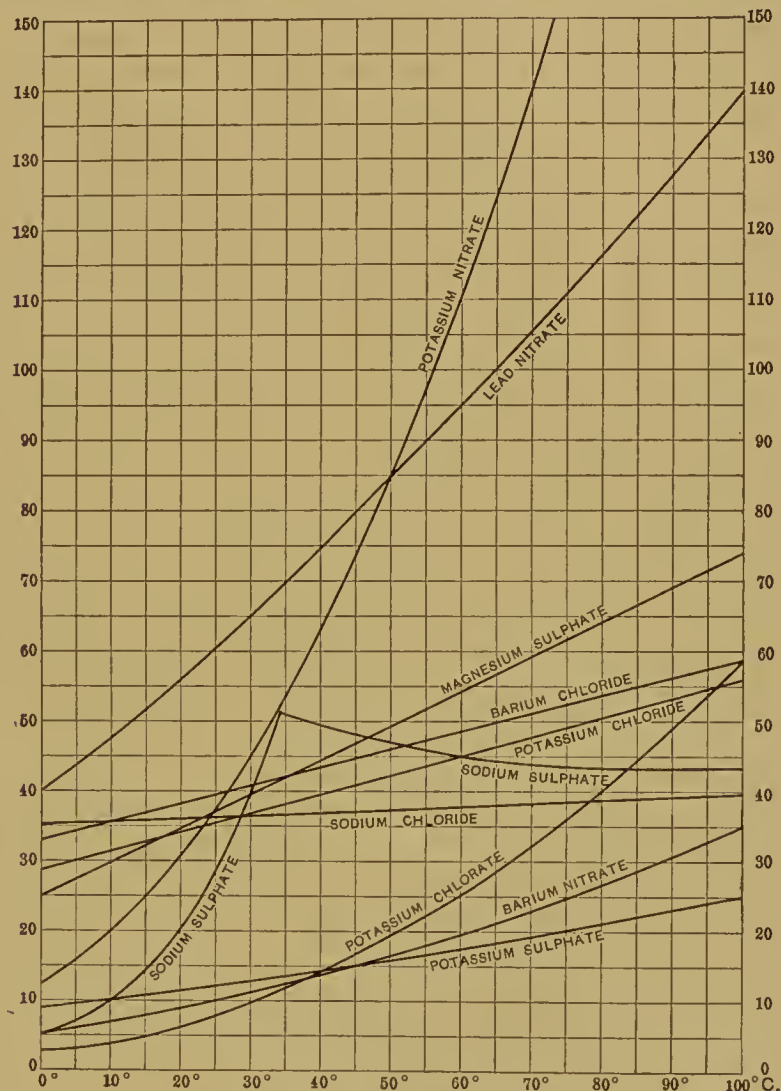


FIG. 66.—SOLUBILITY CURVES.

compound  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ; 1 g.-mol. dissolved in 198 g.-mols.  $\text{H}_2\text{O}$  at  $11^\circ$  gives a caloric effect of + 3.71 Cal.; 19.56 g.-mols. in the same amount of water, - 3.129 Cal.

The heat of solution referred to in VAN'T HOFF'S principle is that of the salt in its saturated solution, for we have the system: salt + saturated solution; when the temperature changes, the equilibrium is displaced, i.e. salt either goes into solution or crystallizes out, the latter producing just as large a numerical effect as dissolving in the saturated solution, but with

the opposite sign. As this was not taken into consideration when the matter was first discussed, it was believed that there were exceptions to the principle, but closer investigation has proved the contrary.

In some cases the solubility of a salt at first increases gradually with rising temperature and then steadily decreases, so that the solubility curve has a maximum (cf. Fig. 67). In full agreement

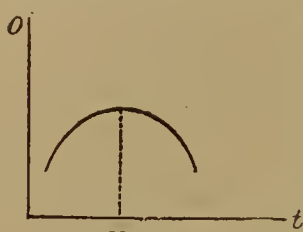


FIG. 67.

with VAN'T HOFF'S principle the heat of solution is negative in the ascending portion of the curve, zero at the maximum and positive in the descending portion. In the case of gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , for instance, the maximum has been found to lie at about  $38^\circ$  and at that point the heat of solution was actually found to be 0.00; at  $14^\circ$

it is  $-0.36$ ; above  $35^\circ$ ,  $+0.24$ .

In regard to the dependence of solubility on pressure it is at most very slight; it is in entire accord with the principle of LE CHATELIER. Ammonium chloride, for instance, dissolves with expansion; therefore its solubility lessens with increasing pressure (1% for an increase of 160 atm.). Copper sulphate, which dissolves with contraction, has its solubility increased 3.2% by an increase of 60 atm. pressure.

**237.** It was formerly thought that the terms "solvent" and "dissolved substance" should be kept distinct. However, it has since developed that there is no essential difference between the parts of a solution and that aqueous solutions are therefore better defined as "liquid complexes, one of whose components is water," than as "water in which substances are dissolved." That there is no such essential difference is evidenced first of all by the phenomena attending the cooling of salt solutions.

Let us assume a nearly saturated solution of potassium chloride at a definite temperature. We have in it two substances ( $\text{KCl}$  and  $\text{H}_2\text{O}$ ) and two phases (§ 71), hence an incomplete equilibrium. We will suppose that the solution is then cooled: potassium chloride crystallizes out forthwith and, as three phases are then present, the equilibrium becomes complete. We recall that changes in the quantity of any phase have no effect on a complete equilibrium; if more salt is introduced into the system, the concentration of saturated solution and vapor are unaffected. This is none the less

true when water is added or the vapor volume increased, so long as the three phases remain.

On cooling still farther, more potassium chloride is gradually deposited until a point is reached when the entire liquid finally congeals to a mixture of salt and ice. This point is known as the **cryohydric, or eutectic, point**.

The opinion was formerly held that at this point a chemical compound between the salt and water (a "cryohydrate") came into existence. That it is only a matter of mixtures can be seen in the case of colored salts ( $K_2CrO_4$ ), for instance, with a microscope; moreover the composition of these so-called hydrates may differ in case the solidification takes place under a different pressure.

If we start with a dilute potassium chloride solution, as another example, and cool it, we have ice formed at a definite moment and thus complete equilibrium established, ice being the third phase required. Below this point *the solution can be regarded as saturated in respect to ice*, just as it could be in respect to the salt in the previous case, for an increase of the solid phase (§ 71) does not cause a displacement of the equilibrium any more than the addition of the solid (salt) did in the previous instance. The addition of potassium chloride causes part of the ice to go into solution (i.e. melt), until that concentration of the liquid phase is reached which corresponds to the temperature at which the solution is kept constant. It is therefore perfectly analogous to the addition of water to a saturated potassium chloride solution in contact with the solid salt, in which case also the solid phase goes into solution. If the temperature rises, more ice dissolves; if it falls, more crystallizes out—just as with rising temperature more potassium chloride goes into solution and with sinking more crystallizes out. On farther cooling more and more ice will be deposited in this case also, until the cryohydric point is reached, when the whole system solidifies to a mixture of salt and ice. The analogy is therefore complete.

The cryohydric point is, according to this view, the point of intersection of two curves, viz.: the solubility curves of the saturated solutions of salt and of ice.

Another argument against the assumption of any essential difference between solvent and dissolved substance (solute) is derived from a consideration of the solutions of certain hydrous salts, e.g.  $CaCl_2 \cdot 6H_2O$ . A saturated solution of  $CaCl_2$  in water at

30.2° has exactly the composition  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . At this temperature, therefore, the hydrate melts to a homogeneous liquid. *If either  $\text{H}_2\text{O}$  or  $\text{CaCl}_2$  is added, there is a deposit of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  on cooling,* for the addition of either causes a depression of the point of solidification (freezing-point) of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . In the first case this hydrate is in equilibrium with a liquid which contains more water than the hydrate does and which is therefore called an aqueous solution in the ordinary sense. In the second it is in equilibrium with a liquid which contains more  $\text{CaCl}_2$  than  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and must therefore be regarded as a solution in  $\text{CaCl}_2$ .

On examining the solubility curves of various salts (cf. Fig. 66) it is found that they are in general regular; however, in one of the curves (Glauber's salt) a sudden change of direction is noticed. This is often observed with salts that contain water of crystallization. Taking Glauber's salt as an example, the phenomenon may be explained thus: It has already been remarked (§ 225) that this salt has a transition-point at the temperature of 33°,  $\text{Na}_2\text{SO}_4 \cdot 10\text{aq}$  being transformed into  $\text{Na}_2\text{SO}_4$  and  $10\text{H}_2\text{O}$ . Up to 33°, therefore, we have the hydrous salt as the solid phase; above this temperature the anhydrous salt. This change must necessarily involve a sudden bend of the solubility curve. Below 33° the curve represents the solubility of  $\text{Na}_2\text{SO}_4 \cdot 10\text{aq}$ , above 33° that of  $\text{Na}_2\text{SO}_4$ . We can therefore also regard the bend in the curve at 33° as the intersection of the curves for  $\text{Na}_2\text{SO}_4 \cdot 10\text{aq}$  and  $\text{Na}_2\text{SO}_4$ . In Glauber's salt the special case appears where the solubility of the anhydrous salt decreases with rising temperature and hence the solubility curve falls as the temperature rises above 33°.

In general, as OSTWALD has pointed out, the solubility of any substance whatsoever is dependent on the condition in which it exists. The solid phase determines the equilibrium, not only by virtue of its chemical composition but also by the particular form in which the solid substance is present. Thus, e.g., each of the various forms of the same polymorphous substance or different hydrates of the same salt has its own solubility, other things being equal.

In a hydrous salt we may have the case where there are various hydrates, which are connected with each other by transition-points. A salt with  $m + n$  molecules of water of crystallization passes over at a definite temperature into another with  $m$  molecules, for example. The latter may, at a higher temperature, have a second

transition-point (to anhydrous salt). At each of these points the solubility curve will show a bend, because the solid phase changes; the curve will therefore assume some such form as that of Fig. 68.

Let us examine such a solubility curve a little more closely. At  $0^\circ$  ( $A$  in Fig. 68) we will suppose we have pure water and ice, to start with, and that small portions of salt are then gradually dissolved. If the ice phase is to be preserved, the temperature must be allowed to sink, for a salt solution has a lower freezing-point than pure water. We therefore move along the curve  $AK$ . Soon a

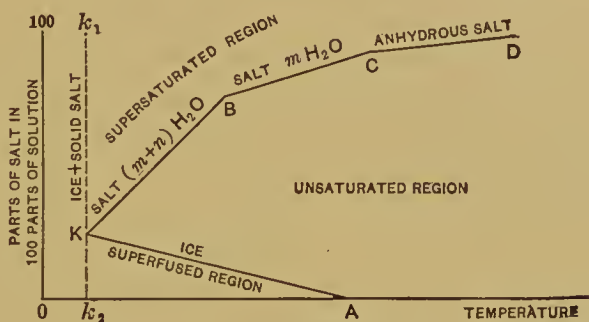


FIG. 68.

point  $K$  is reached when no more salt dissolves, since all the water has now turned to ice. Here, therefore, we have a mixture of ice and solid salt, or, in other words, the cryohydric point.

If we wish to bring more salt into solution after  $K$  is reached, the temperature must be raised. The ice phase then, of course, disappears and in its place we have the salt with  $(m+n)$  molecules of water of crystallization at the bottom. If the solution is kept constantly saturated by the addition of this salt, we move along the curve  $KB$ . At  $B$ , however, we meet the transition-point from the salt with  $(m+n)$  mols.  $H_2O$  to the one with  $m$   $H_2O$ ; hence the solubility curve must again bend here and in such a way that at the point  $B$  the solubility curve of the salt with  $(m+n)$  mols.  $H_2O$  is steeper than that of the salt with  $m$  mols., no matter what the form of the curves  $KB$  and  $BC$  may be. This is at once made clear by a course of reasoning entirely analogous to that given for the transition of ice to water or of rhombic to monoclinic sulphur (§ 70). Finally at  $C$  we have a second transition-point from salt with  $m$  mols.  $H_2O$  to anhydrous salt, so that the solubility curve there shows one more bend. Where the curve  $CD$  ends depends on circum-

stances. In many cases, e.g. that of silver nitrate, it ends at the melting-point of the anhydrous salt (concentration of the solution = 100%). In other instances the anhydrous salt can form a second (fused) liquid layer under the saturated solution. Finally, mention may be made of the case of copper sulphate, which at a given temperature loses its water of crystallization in contact with its saturated solution and from that point on shows a decrease in solubility with rising temperature, which finally ends in almost total insolubility.

If we draw a line  $k_1k_2$  through  $K$  parallel to the ordinate axis, the figure is divided by this line and  $AKBCD$  into the following regions: To the right of the solubility curve is the region of the unsaturated solution,  $AKk_2$  is that of the superfused,  $k_1KBCD$  that of the supersaturated solutions. To the left of  $k_1k_2$  only ice + solid salt can exist under ordinary pressures.

**Supersaturated solutions.** A Glauber's salt solution saturated a little below  $33^\circ$  can, if carefully guarded from contact with any of the solid salt, be cooled down to room-temperature without anything crystallizing out, but contact with the tiniest crystal fragment of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is sufficient to cause a sudden crystallization of this salt.

Besides Glauber's salt there is a whole series of salts that can form solutions having this property, e.g. sodium thiosulphate, many nitrates, etc. Such solutions are called *supersaturated*. They are perfectly stable; they can be shaken or rubbed with a glass rod (which ordinarily can greatly promote crystallization) without the formation of crystals, provided no trace of the solid salt comes in contact with the solution. Such a system, which is thus *unstable under only one condition*, is called a **metastable system**.

If a supersaturated solution of Glauber's salt is cooled down below room-temperature, another hydrate crystallizes out, viz.,  $\text{Na}_2\text{SO}_4 \cdot 7\text{aq}$ ; the resulting system is still metastable, for even now contact with the slightest trace of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  suffices to convert it entirely into the stable system with the deposition of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

The amount of salt that is sufficient to cause the disappearance of a metastable system, such as is represented by a supersaturated solution, is a quantity of about the order  $10^{-10}$  g, according to OSTWALD. The extreme minuteness of this amount explains how it could formerly be supposed that a spontaneous disappearance of the metastable condition

was possible. Inasmuch as very small bits of crystals are always floating in the air (especially in laboratories), it is usually only necessary to open a bottle containing a supersaturated solution, in order to excite crystallization into the stable system.

238. For the reasons stated in §§ 65 and 66 it is assumed that acids, bases and salts in aqueous solution are split up into ions. This dissociation can be more or less complete, according to the nature of the solute, the temperature of the solution and its concentration. Examples of this have already been mentioned here and there; hydrochloric and nitric acids in tenth normal solutions are almost completely dissociated, carbonic and silicic acids scarcely at all; among the bases the hydroxides of potassium, sodium and the alkaline earths are almost completely dissociated in this dilution. This same difference is shown by the salts; those of the alkalis are as good as completely ionized, while mercuric chloride is very slightly so. We shall return to this subject more in detail in the discussion of the metals.

The principle that solutions containing equivalent amounts of different electrolytes differ greatly in conductivity and hence in degree of ionization can be demonstrated in an elegant manner with the aid of an apparatus devised by W. R. WHITNEY (Fig. 69).

Four glass cylinders (3 cm. diam.) are fitted each with two horizontal platinum disks (copper can be used but is less satisfactory) to serve as electrodes, the upper ones being movable. Each lower electrode is connected with an incandescent lamp and the apparatus as a whole with the terminals of a (preferably) alternating 110-volt circuit. After placing in the tubes 120 cc. distilled water each they are filled with 5 cc. of half-normal hydrochloric, sulphuric, monochloroacetic and acetic acids respectively. On making the distance between the electrodes alike in all the cylinders, the lamp beneath the hydrochloric acid is found to glow brightest, since the resistance of this solution is the least. The other lamps follow in brightness in the order given above. The electrodes are next adjusted so that all the lamps are equally bright, when it is seen that while the electrodes in the hydrochloric acid are farthest apart, those in the acetic acid are almost in contact.

In order to show that the alkali salts of these acids, unlike the acids themselves, have nearly the same conductivities and degrees of dissociation the solutions are neutralized with potassium hydroxide and the lamp test repeated. The lamps are equally brilliant when the electrodes are at approximately the same heights.

The dissociation theory furnishes an explanation of many physical phenomena of solutions which had been observed before

this hypothesis was advanced but which were not understood. We may mention a few:

1. *The heat of neutralization is nearly the same for all strong*

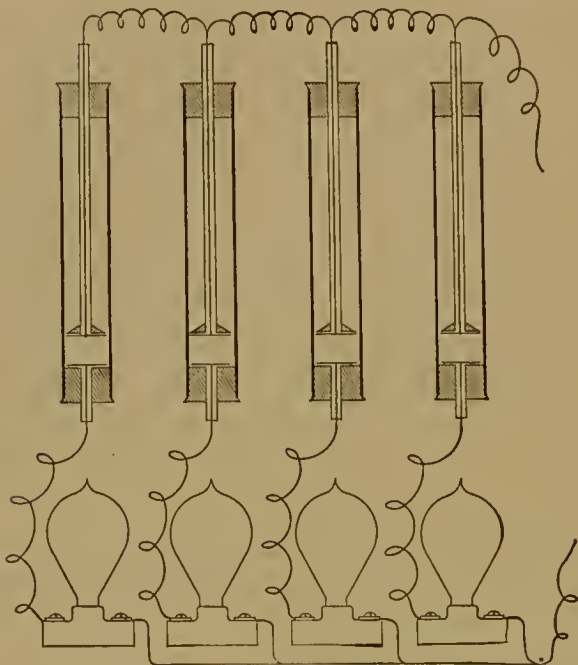


FIG. 69.

*acids and bases.* This is seen from the following brief table giving the caloric effect of neutralization for different acids and bases:

	HCl (HBr, HI)	HNO <sub>3</sub>	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> Acetic Acid.	$\frac{1}{2}$ H <sub>2</sub> S
NaOH.....	+ 13.7	+ 13.7	+ 13.3	+ 3.8
KOH.....	+ 13.7	+ 13.8	+ 13.3	+ 3.8
$\frac{1}{2}$ Ca(OH) <sub>2</sub> .....	+ 14.0	+ 13.9	+ 13.4	+ 3.9
$\frac{1}{3}$ Ba(OH) <sub>2</sub> .....	+ 13.8	+ 13.9	+ 13.4	.....
$\frac{1}{2}$ Sr(OH) <sub>2</sub> .....	+ 14.1	+ 13.9	+ 13.3	.....
NH <sub>4</sub> OH.....	+ 12.4	+ 12.5	+ 12.0	+ 3.1

The theory explains this as follows: The bases and acids in question are almost completely dissociated into ions in dilute solution. The formation of a salt must therefore be represented by the equation :





i.e. the ions  $H'$  and  $OH'$  unite to form water, which is only slightly dissociated into ions, while  $M'$  and  $A'$  remain in the free state just as before the mixing of base and acid. The only thing that occurs in the process of salt-formation in dilute solutions is the union of hydrogen and hydroxyl ions to form water, no matter which (strong) bases and acids are brought together. The heat of neutralization for weaker acids (acetic acid,  $C_2H_4O_2$ , and hydrogen sulphide) is different (see table), since more processes are involved in the formation of the salt in these cases than simply the production of water; in neutralizing with weak acids the separation of the ions requires a certain heat expenditure. In the formation of a salt from ammonia water a caloric effect is produced by the addition of ammonia to the acid and another by the subsequent ionization of the salt.

2. On mixing dilute solutions of the salts of strong bases and acids no caloric effect is to be observed. This is the **law of thermo-neutrality**. When considered from the standpoint of the ionic theory, it becomes at once intelligible: When the salts are mixed, they remain completely dissociated; no reaction whatsoever takes place, that could produce a heat effect.

3. On mixing strong acids and bases in dilute solution the same change of volume results in each case, according to OSTWALD. The following table gives the volume change in cubic centimeters for different combinations, when 1 kg. liquid containing 1 gram-equivalent of acid is mixed with 1 gram-equivalent of base, also diluted to 1 kg. liquid. (+ indicates an increase, — a decrease, in volume.)

	KOH	NaOH	NH <sub>4</sub> OH
HNO <sub>3</sub> .....	+ 20.05 cc.	+ 19.77 cc.	— 6.44 cc.
HCl.....	+ 19.52	+ 19.24	— 6.57
HBr.....	+ 19.63	+ 19.34	— 6.57
HI.....	+ 19.80	+ 19.56	— 6.44

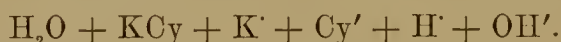
For the strong bases KOH and NaOH we find there is nearly the same expansion in each case. When the base is ammonia, however, the process of salt formation is of a different nature and a contraction is observed on mixing the components.

4. If an acid or a base forms salts whose aqueous solutions are

eolored, this eolor is the same for all salts whose other ion is colorless (OSTWALD). This is illustrated by the salts of permanganic acid and certain organic acids, for instance, which give exactly the same absorption spectrum in equivalent dilute solutions. If we assume that it is the anion of the acid which gives the eolor to the liquid, the phenomena are at once understood.

When the solvent is one in which ionization does not occur, the salts of the same base may differ widely in color. For instance, a solution of cobalt nitrate in alcohol is purple, that of the chloride is bluish violet; but if both are poured into an excess of water, the solution becomes pink in each case. Another example is found in the alcoholic solutions of copper chloride and nitrate; the first is dark green, the latter blue; on addition of water both become blue.

**239.** A large number of salts are known which have a basic or acid reaction in aqueous solution. Examples of the former were met with in the carbonates of the alkalies, potassium cyanide, etc.; aluminium sulphate is an example of the second sort. The salts of many heavy metals, also, react acid. All such salts have the common property of being derived either from a weak acid or a weak base. The theory of electrolytic dissociation supplies the following explanation of this phenomenon: Let us take a solution of potassium cyanide for example; here there are undissociated KCy molecules and K and Cy ions present and farther a very small amount of H and OH ions, because the water also is broken up into ions to a very slight extent. We thus have in the solution



Now the ionization of prussic acid is extremely slight. As Cy and H ions are present side by side, they unite to form HCy molecules, until the equilibrium between HCy and its ions is established according to the existing dilution. The result is that more water molecules must be ionized, so that more OH ions (which are in equilibrium with the K ions) than H ions enter the solution. The acid reaction due to the latter is much more than counteracted by the alkaline reaction of the former since the concentration of the H ions is less (§ 66); hence the liquid gives an alkaline reaction. The acid reaction of salts of weak bases can be explained in an exactly analogous manner.

This breaking up of a salt into free acid and free base under the action of water is termed **hydrolytic dissociation**; it is especially apt to occur with salts which have a weak base and also a weak acid, for in such a case not only do the anions of the salt combine with the H ions of the water but the cations also combine with the OH ions of the latter. However, if one of the components has a certain strength, as, e.g. the base in the case of KCy just considered, the OH ions remain free and the ionization of the water is greatly diminished by the large proportion of OH ions. As a result the hydrolytic dissociation cannot proceed very far.

This hydrolytic dissociation underlies a number of phenomena in analytical chemistry. When a solution of a chromium or aluminium salt is treated with ammonium sulphide or carbonate, we should expect the sulphide or carbonate of chromium or aluminium to be formed, but, inasmuch as the base as well as the acid is weak, the great excess of water causes a complete dissociation of these salts so that hydrogen sulphide or carbon dioxide escapes and the base is deposited.

If ammonium chloride is added to an alkaline solution of aluminium hydroxide, the latter is precipitated, thus behaving as an extremely weak acid; hence the ammonium aluminate suffers complete hydrolytic dissociation. For the same reason free silica is precipitated by ammonium chloride from the solution of an alkali silicate. In both cases the action is aided by the fact that the ammonium hydroxide which is primarily formed in the hydrolysis splits up almost entirely into ammonia and water (§ 234).

The conduct of silver borate is interesting. On treating a concentrated solution of an alkali borate with silver nitrate, white silver borate is deposited. In a dilute solution, however, silver borate gives a grayish brown precipitate of silver oxide; it follows from this that a great excess of water is required to effect the complete hydrolysis of silver borate.

### Acidimetry and Alkalimetry. Theory of Indicators.

**240.** The amount of acid or base present in a liquid can be determined most simply by volumetric analysis (§ 93). That part of volumetric analysis which comprises the methods used for this purpose is known as *acidimetry and alkalimetry*. Suppose that we

wish to determine the amount of hydrochloric acid present in a given volume of liquid. A known volume of this liquid (50 cc., 10 cc., or less, according to the supposed concentration) is measured out and sodium hydroxide solution of known concentration is slowly added from a burette. When the point has been found at which the liquid becomes neutral, it is easy to calculate the concentration of the acid from the number of cubic centimeters of sodium hydroxide consumed.

*Example.* Determine the amount of nitric acid present in a liter of a solution of this acid if 10 cm.<sup>3</sup> are neutralized by 7.3 cm.<sup>3</sup> of a normal alkali solution. These 7.3 cm.<sup>3</sup> are equivalent to the same number of cubic centimeters of normal nitric acid. Therefore the 10 cm.<sup>3</sup> contain 7.3 milligram molecules of nitric acid or  $63 \times 7.3$  mg. One liter must contain a hundred times as much, or 45.99 g.

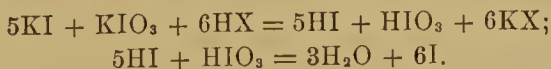
Before we can determine the concentration of an acid or an alkali in this manner, we must first possess an alkali or base solution of known concentration and farther have a delicate means of detecting when the liquid is exactly neutralized.

1. *Preparation of an acid and an alkali of known concentration.* This can be done in various ways. Oxalic acid,  $C_2H_2O_4 + 2H_2O$ , succinic acid,  $C_4H_6O_4$ , or tartaric acid,  $C_4H_6O_6$ , can be used as the basis, for all of these are crystallized solids and can be easily obtained in a state of sufficient purity; hence the amount of acid dissolved can be very accurately determined by previously weighing the substance on an analytical balance. We thus weigh out 1 g.-equivalent ( $\frac{1}{2}$  g.-mol.) of one of these acids, dissolve it in water and dilute to exactly a liter. Thereupon with the help of this normal acid a normal alkali is prepared: a little more than 1 or  $\frac{1}{2}$  or  $\frac{1}{10}$ , etc., equivalent of sodium hydroxide or potassium hydroxide (barium hydrate is also very satisfactory) is dissolved in water and this solution is standardized according to the normal acid, i.e. the concentration is determined by titration with normal acid and then diluted so that it is just normal.

Sodium carbonate can also be used as a basis. After being first heated in order to expel all moisture it is weighed out and dissolved in water. This solution is heated to boiling and covered with a glass plate with a hole in it through which the point of a burette is passed. The solution of the acid whose concentration is to be determined is then allowed to flow from the burette into the boiling liquid till neutralization is effected;

carbon dioxide escapes, but the glass plate prevents any loss of the liquid by spurting.

The standardizing can also be accomplished by adding the acid solution that is to be standardized to a mixed solution of KI and KIO<sub>3</sub>. HI and HIO<sub>3</sub> are set free and they react at once in the following manner :



Thus for every equivalent of acid one atom of iodine is set free. By titrating with sodium thiosulphate the amount of iodine liberated can be determined. This method gives very accurate results.

2. *Determination of the point at which the liquid becomes neutral.* Since the point of neutralization of an acid by a base or *vice versa*, is not indicated by any visible phenomena, a minute quantity of some substance is added whose color is altered by an excess of the neutralizing liquid. Such substances are *litmus* (blue in alkaline and red in acid solutions), phenol-phtalein (red in alkaline, colorless in acid), *methyl orange* (yellow in alkaline, red in acid) and many others. Therefore on gradually adding an  $\frac{\text{alkaline}}{\text{acid}}$  solution to an  $\frac{\text{acid}}{\text{alkaline}}$  solution in the presence of one of these substances a *change of color* will be noticed when the point of neutrality is just passed. Coloring-matters like the above are termed **indicators**. They are mostly of a feebly acidic character (in a few cases slightly basic). The change of color depends on their transformation into salts which have a different color than the free acid.

241. From the standpoint of the ionic theory the following **theory of indicators** has been advanced: If a couple of drops of the indicator are introduced into an acid solution the ionization of the indicator, which is only very feeble, is reduced by the great excess of acid to practically zero. If a base is then added, the H ions of the acid to be titrated are removed by the OH ions. However, if the acid is very strong, enough H ions remain in the liquid up to the last to prevent any thing like an extensive ionization of the coloring-substance; not until the first excessive drop of alkali is added do the anions of the coloring-substance come into existence, the alkali compound of the latter being strongly dissociated. *The change of color is therefore sharply defined*, for it is due to this difference in color of the non-ionized molecule and the

anion. On the contrary, if the acid is a weak one, there will not be enough H ions present when the end of the titration is nearly reached to prevent a slight ionization of the coloring-substance. As a result we shall have in the solution not only the undissociated coloring-substance but its anions as well, even before the titration is completed,—in other words, *the change of color becomes more gradual* and hence the end reaction more indefinite. The effect must be the same if the alkali employed contains carbonate. In that case near the end of the titration the solution will only contain carbonic acid, which is very weak; consequently the color change is not sudden. It is for this reason that in titrating soda solutions (see § 240) the carbonic acid must be eliminated by boiling.

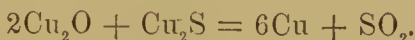
If a weak acid is to be titrated, it is necessary, according to the above, to select an indicator which is much less ionized even than the acid itself and whose alkali salts are sufficiently ionized to produce a distinct change of color. A very suitable one for this purpose is phenolphthaleïn. Acetic acid, for example, can be satisfactorily titrated with it, if a strong base is employed, for the reasons set forth above. On the other hand, in case a weak base is to be titrated, phenol-phthaleïn is not so satisfactory. Ammonia does not color a phenol-phthaleïn solution till a considerable excess is added, because at the great dilution in which its ammonium compound exists in a titration it is almost completely split up by hydrolysis (§ 239).

If a weak base is to be titrated, an indicator must be selected which is a relatively strong acid, for then the salt of the coloring-substance will be hydrolyzed only to a limited extent, even near the termination of the titration (i.e. when the concentration of the base has become weak), and therefore the color of its ions will still predominate. For such a titration a strong acid (e.g. hydrochloric or sulphuric acid) must be used in order that the first drop after the moment of neutralization may diminish the electrolytic dissociation of the coloring-substance and so give the solution the color of the non-ionized molecules. *Methyl orange* is an indicator that answers these requirements; it serves very well in the titration of ammonia. All other indicators are intermediate to these two extremes (phenol-phthaleïn and methyl orange) as regards their ionization and their applicability is determined accordingly.

## COPPER.

242. This metal occurs *native* in America, China and Japan, forming regular crystals. Other copper minerals are *cuprite* ( $\text{Cu}_2\text{O}$ ), *malachite* and *azurite* (both basic carbonates), *chalcocite* ( $\text{Cu}_2\text{S}$ ) and particularly *chalcopyrite*, or *copper pyrites*, ( $\text{CuFeS}_2$ ).

The extraction of the metal from non-sulphurous ores is very simple. They are smelted with coal and thus reduced to the metallic state. If the copper ore contains sulphur, the metallurgical process is much more complicated and has numerous modifications. The ore is broken up and "calcined" so as to convert some of the copper sulphide into copper oxide. Thereupon it is fused with sand and other siliceous fluxes, as well as coal for reducing copper sulphate, whereby the iron but not the copper is converted into silicate. The object of the flux, here as with other metals, is to lower the fusing temperature of the ore and collect the impurities (iron in this case) into a "slag" consisting of fused silicates, etc. The slag floats and can be run off. The fusion process is repeated until all the iron is eliminated. The resulting mixture of impure copper sulphide and copper oxide is called *matte* (also *regulus* and *coarse metal*). By repeated roasting and fusing, crude metallic copper is obtained:



Finally it is fused with coal to reduce any copper oxide remaining.

Refining. The copper thus obtained often contains small quantities of other metals. Since these impurities lower its conductivity a better grade is demanded for electrical purposes. Crude copper is now refined by an *electrolytical process* which yields chemically pure copper. If an impure copper solution is electrolyzed it is possible under certain circumstances to precipitate pure copper in a compact mass, while the impurities remain in solution or are deposited as powder. From these "slimes" a considerable amount of gold and silver is obtained.

The usual arrangement is to suspend plates ("anodes") of crude copper and thin sheets of pure copper alternately in a copper vitriol solution acidified with sulphuric acid. If the crude plates are then connected with the positive pole and the thin sheets with the negative pole of the dynamo current, pure copper is deposited on the sheets while an equivalent amount of the crude copper dissolves to take its place. In 1900 the estimated daily production of electrolytically refined copper in the United States was 573 metric tons (one-half the world's copper output).

*Physical Properties.* Copper has a bright red color. It is rather hard but very extensible and flexible; it can be drawn out into very fine wire and beaten into extremely thin sheets (imitation gold-leaf), which are green in transmitted light. Sp. g. = 8.94; melting-point =  $1045^{\circ}$ .

*Chemical Properties.* In dry air copper is permanent at ordinary temperatures, but in moist air it becomes covered with a thin coating of basic copper carbonate, which protects it from further rusting. On being heated in the air it turns to copper oxide,  $\text{CuO}$ . It is easily corroded by nitric acid (§ 120), but not by dilute hydrochloric acid. Sulphuric acid has no effect on it at ordinary temperatures, but at higher temperatures a reaction takes place in which sulphur dioxide is given off (§ 78). Ammonia and oxygen dissolve it to form a blue liquid, copper oxide-ammonia. Copper is deposited from solutions of its salts by iron, magnesium, etc.

*Uses and alloys.* Copper finds extensive use in the arts, both as such and in alloys. The well-known yellow brass is an alloy of 1 part zinc and 2 parts copper and is harder than copper itself. German silver consists of about 50% Cu, 25% Ni and 25% Zn; its electrical conductivity is affected very little by changes of temperature, which makes it valuable for resistance coils, etc. For bronzes see § 199.

Copper is employed in large quantities in electrotyping. A cast is first constructed of plaster of Paris and made a conductor by coating it with graphite, whereupon it is suspended by the wire of a battery into a copper sulphate solution; a plate of pure copper serves as the anode. If the potential difference at the electrodes is properly regulated, the copper is deposited on the plaster cast in compact form, so that all the details of the original are reproduced with the greatest fidelity.

### Compounds of Copper.

243. Copper forms two sets of salts, which are derived from the oxides  $\text{Cu}_2\text{O}$ , *cuprous oxide*, and  $\text{CuO}$ , *cupric oxide*.

#### CUPROUS COMPOUNDS.

**Cuprous oxide**,  $\text{Cu}_2\text{O}$ , can be obtained from cupric salts in various ways, e.g. by reducing in alkaline solution with grape sugar, hydroxylamine, arsenious acid, or the like. It forms a



reddish-yellow crystalline powder, which is unaffected by the air at ordinary temperatures. It dissolves in ammonia; this solution rapidly turns blue because of the absorption of oxygen, the cuprous oxide going over into cupric oxide. Cuprous oxide is transformed by sulphuric acid into copper sulphate and copper:



It is possible that cuprous sulphate is first formed and that the cuprous ions of this solution are forthwith changed into cupric ions and non-ionized copper,  $2\text{Cu}' = \text{Cu}'' + \text{Cu}$ .

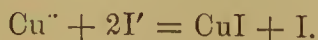
Of the **cuprous salts** only those of the halogens are known.  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}_2\text{Br}_2$  and  $\text{Cu}_2\text{I}_2$  are all "insoluble" (cf. § 235); their solubility decreases with increasing atomic weight of the halogen.

**Cuprous chloride**,  $\text{Cu}_2\text{Cl}_2$  (the vapor density indicates this doubled formula), is formed when a solution of cupric chloride is boiled with copper, or when a mixed solution of copper sulphate and sodium chloride is saturated with sulphur dioxide gas and the resulting liquid poured into water. It is a white crystalline substance, which must be kept under water, for it absorbs oxygen rapidly when moist and turns green from the formation of basic copper chloride,  $\text{CuCl}\cdot\text{OH}$ . It melts at  $430^\circ$  and distills at ca.  $1000^\circ$ . It is soluble in concentrated hydrochloric acid and ammonia. These solutions are at first colorless but very soon become blue because of the absorption of oxygen (formation of cupric compounds). They also have the power of absorbing carbon monoxide, forming an unstable compound,  $\text{Cu}_2\text{Cl}_2\cdot\text{CO}\cdot 2\text{H}_2\text{O}$ , which crystallizes in colorless laminae, and they are therefore used to absorb this gas in gas analysis.

**Cuprous iodide**,  $\text{Cu}_2\text{I}_2$ , is formed when a solution of copper sulphate is treated with potassium iodide, half of the iodine being liberated:

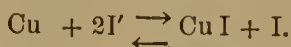


It may be supposed that in the very first stage cupric iodide (with the ions  $\text{Cu}''$  and  $\text{I}'$ ) is formed and that the bivalent cupric ion is then converted into the univalent cuprous ion:



According to OSTWALD, however, an equilibrium is formed here, since the reaction does not complete itself and copper still remains in solution.

This follows from the fact that cuprous iodide is dissolved by an alcoholic iodine solution. We therefore have:



If we remove one of the reaction products, the liberated iodine (e.g. by sulphur dioxide), the reaction will be able to complete itself and the more so as iodine is converted into I ions; the concentration of one of the components on the left side of the equilibrium equation is thus raised, so that the deposition of the scarcely soluble salt is made more complete.

**Cuprous cyanide**,  $\text{Cu}_2\text{Cy}_2$ , can be obtained in a manner analogous to that described for cuprous iodide, viz., by mixing solutions of copper sulphate and potassium cyanide. Half of the cyanogen escapes as gas:



Cuprous cyanide dissolves very readily in an excess of potassium cyanide, forming a salt,  $2\text{KC}_y \cdot \text{Cu}_2\text{Cy}_2$ , which contains a complex anion  $(\text{Cu}_2\text{Cy}_4)''$ . Practically all of the copper ions go to form these complex ions on the addition of potassium cyanide, for the solution gives none of the ordinary reactions for copper, not even that with hydrogen sulphide, although copper sulphide is precipitated by it even when the concentration of the copper ions is very slight (§ 73).

#### CUPRIC COMPOUNDS.

**244. Cupric oxide**,  $\text{CuO}$ , is a dense black powder, obtained by heating copper in the presence of oxygen at a high temperature. It can also be prepared by igniting the nitrate till it glows or heating the hydroxide or the carbonate. When finely divided it occludes on its surface large amounts of steam. It finds extensive use in organic analysis.

**Cupric hydroxide**,  $\text{CuO} \cdot n\text{H}_2\text{O}$ , separates out as a flocculent, voluminous blue precipitate (hydrogel, § 195) when the solution of a copper salt is treated with caustic potash or soda. On boiling the liquid it turns black, water being liberated and cupric oxide formed.

**Cupric chloride**,  $\text{CuCl}_2 + 2\text{H}_2\text{O}$ , is obtained by dissolving cupric oxide or carbonate in hydrochloric acid. It crystallizes in blue rhombic needles, which, however, often appear green because of mother liquor adhering to them. It is readily soluble in water

and alcohol. The anhydrous salt is yellow; the concentrated aqueous solution is green; the dilute solution is blue. This difference can be attributed to the breaking up of the salt into its ions, for all dilute copper solutions are blue, no matter what the acid radical is. It therefore follows that the copper ion imparts a blue color to solutions. In a concentrated solution of cupric chloride the yellow color of the undissociated molecules forms with the blue of the copper ions a green color.

The following phenomenon is rather peculiar. If water is added to a solution of cupric chloride till it is just blue and the liquid is then warmed, the color changes to green. According to the above explanation of the change of color the electrolytic dissociation must diminish on warming, wherefore, in accordance with the principle of mobile equilibrium (§ 235), the heat of ionization must be positive, in other words, heat must be evolved when the salt splits up into its ions. Experiments by ARRHENIUS have shown this to be true for certain salts, e.g. copper sulphate, so that it may also be assumed here.

On mixing a copper sulphate solution with a concentrated sodium chloride solution the color turns green because of the formation of  $\text{CuCl}_2$  molecules. We should therefore expect this same result when an excess of chlorine ions is introduced into any copper solution, and experience has shown this to be the case.

Cupric bromide is analogous to the chloride; cupric iodide is unstable, decomposing at once into iodine and cuprous iodide (§ 243).

Copper sulphate,  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ , blue vitriol, is the most familiar salt of copper. It is obtained as a by-product, chiefly from gold and silver refineries, and is also manufactured by dissolving copper in sulphuric acid. It crystallizes in large blue triclinic crystals, which lose four molecules of water at  $100^\circ$ ; the fifth is liberated at  $200^\circ$ . The anhydrous copper sulphate is a white powder, which absorbs water greedily, turning blue again. At  $20^\circ$  100 parts  $\text{H}_2\text{O}$  dissolve 42.31 parts of the crystallized sulphate. Blue vitriol is employed in large quantities in electroplating, etc. (§ 242).

Copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , can crystallize with three or six molecules of water and is dark blue.

Copper carbonate. The normal salt is unknown, but basic salts have been prepared.

**Copper arsenite**,  $\text{CuIIAsO}_3$ , is used as a pigment under the name of *Scheele's green*; *Schweinfurth green*, or *Paris green*, is a double compound of copper arsenite and copper acetate. Since both are very poisonous, their use in dyeing textile fabrics, wall paper, etc. (§ 157) is being restricted.

**Copper sulphide**,  $\text{CuS}$ , is formed as a black precipitate by passing hydrogen sulphide into a copper solution. When moist it oxidizes slowly in the air to copper sulphate. On being heated in a current of hydrogen it yields cuprous sulphide,  $\text{Cu}_2\text{S}$ , and hydrogen sulphide.

*Copper salts and ammonia.* On mixing a solution of ammonia with a copper salt, a precipitate of copper hydroxide is first formed, if not too much ammonia is used; this precipitate is dissolved by an excess of ammonia to a dark blue solution. If the latter is evaporated or treated with alcohol, ammoniacal compounds crystallize out; a typical one is  $\text{CuSO}_4 + 4\text{NH}_3 + \text{H}_2\text{O}$ , which is transformed into  $\text{CuSO}_4 + 2\text{NH}_3$  on heating to  $150^\circ$ . The aqueous solutions of these substances are to be assumed to contain complex ions of copper and ammonia, since they do not give some of the ordinary copper reactions, e.g. precipitation with caustic potash. The fact that certain other reactions of copper do however appear, e.g. precipitation with hydrogen sulphide, proves that free copper ions are still present in the liquid, although only to a small extent.

## SILVER.

**245.** This metal occurs *native*; nuggets weighing 100 kilos are not unknown. The important silver ores are *argentite*,  $\text{Ag}_2\text{S}$ , *stromeyerite*,  $\text{Cu}_2\text{S} \cdot \text{Ag}_2\text{S}$ , *pyrargyrite*,  $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ , and *stephanite*,  $\text{Ag}_5\text{S}_4\text{Sb}$ . It is also found in smaller amounts in *cerargyrite*, or *horn silver*,  $\text{AgCl}$ . Traces of silver compounds are known to exist in sea-water. Many lead ores, e.g. galenite, contain a small percentage of silver and in some cases it is extracted.

The chief silver-producing countries are the United States (Colorado and neighboring states), Mexico, Australia and Bolivia.

The *metallurgy* of silver is rather complicated; several processes are employed.

(1) The sulphurous ores are roasted in the air, whereby the

sulphate,  $\text{Ag}_2\text{SO}_4$ , is formed. This is extracted with water and the silver precipitated from the solution by iron.

(2) The ores containing free silver are roasted with common salt, thus yielding silver chloride. The latter is then brought into solution by means of sodium thiosulphate and sodium sulphide is added to precipitate the sulphide of silver. This is then converted into the metal by heating at a high temperature.

(3) *Amalgamation Process.* In Mexico, where there is lack of fuel, the ores, finely powdered, are stirred into water and treated with sodium chloride; this mud is intimately mixed by spreading it out on a floor (*Patio*) and making mules tread it out. Thereupon some mercury is added, as well as a mixture of ferric and cupric salts, and the whole is worked over thoroughly for several days. The liberated silver forms an amalgam with the mercury and can be obtained by distilling off the mercury. In the above process the following reactions probably take place:



The cuprous chloride,  $\text{Cu}_2\text{Cl}_2$ , dissolves in the brine and reacts with another portion of silver sulphide:



The silver chloride dissolves in the brine and the silver is precipitated from solution by mercury, which goes over into calomel.

(4) Lead ores usually contain some silver. In the smelting of lead the silver all goes into the lead and is recovered from it in the following way: The argentiferous lead is fused and then cooled slowly till it begins to congeal. Just as pure ice crystallizes out of a dilute salt solution on cooling, so the lead separates out here in crystals free from silver. These are removed and this process—called *Pattinsonizing* after its inventor—is kept up till the percentage of silver reaches about 1%. This rich lead is then subjected to the *cupellation* process, i.e. the lead is fused in a reverberatory furnace, whose hearth consists of a porous mass (cupel, or test). The lead is oxidized to the easily fusible oxide  $\text{PbO}$  (litharge) which is partly driven off by a blast from time to time through the channel provided for its escape and partly absorbed by the porous material (bone-ash, or clay and limestone) of the cupel. Towards the end of the process the film of litharge remaining becomes so

thin that the silver beneath reflects the light, producing a beautiful iridescence. Here and there the film breaks, disclosing the brilliant surface of the metal ("brightening" of the silver). The silver is finally left in the metallic state.

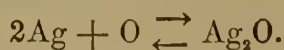
Another method (PARKES') is based on the facts that silver dissolves very readily in molten zinc and zinc only slightly in molten lead. The fused lead can therefore be extracted with fused zinc (cf. Organic Chem. § 24). The process is as follows: To the fused argentiferous lead some zinc (containing 0.5% Al) is added and the mixture stirred. The zinc takes up most of the silver from the lead and floats on the molten mass. It is skimmed off and cast into plates, which serve as the anodes in the subsequent electrolysis. At the cathode nearly pure zinc is deposited, while silver powder (70-80% Ag, the rest Pb) sinks to the bottom and is removed to the anode.

The electrolytic refining of silver is now carried on extensively in America. About 52,000 oz. Troy is recovered daily from the copper slimes (§ 242).

The pure silver of commerce usually contains a little copper and other metals; STAS obtained it chemically pure by dissolving the product of the smelter in nitric acid and precipitating it with hydrochloric acid as the chloride; this was then reduced by boiling with dilute caustic potash and milk sugar and finally distilled with the aid of an oxyhydrogen flame in an apparatus made of lime.

*Physical Properties.* Silver crystallizes in regular octahedrons; it has a white color and a high lustre; it is the best conductor of heat and electricity of all the metals and it is very malleable and ductile. Sp. g. = 10.5; m.-pt. = 954°; at an elevated temperature it volatilizes in the form of a blue vapor (STAS). Molten silver absorbs oxygen, but allows it to escape on becoming solid (§ 9).

*Chemical Properties.* Silver is one of the precious metals; this term is applied chemically to those metals which do not combine with oxygen directly (under ordinary pressure) either at ordinary or higher temperatures. If, however, the pressure is raised, silver combines with oxygen directly at an elevated temperature:



Nitric acid attacks it readily at ordinary temperatures, sulphuric

acid only at higher temperatures; hydrochloric acid has very little effect on it.

*Uses; alloys.* Pure silver is seldom made use of practically, but its alloys are employed in the manufacture of silverware and coins. For these purposes an alloy with copper is used. Silver plate and jewelry usually contain 75 or more per cent of silver; the silver coins of the United States and continental countries consist of 90% silver and 10% copper; the English shillings ("sterling" silver) contain 92.5% silver. The admixture of copper makes the metal harder.

Considerable silver is consumed in silvering objects of copper or other metals (silver-plating). At present this is usually done by electrolysis (§ 242). The object to be plated is made the cathode and a silver plate the anode; the solution consists of silver cyanide dissolved in an excess of potassium cyanide.

### Compounds of Silver.

**246.** The known oxides are:  $\text{Ag}_4\text{O}$ , *silver suboxide* (very unstable);  $\text{Ag}_2\text{O}$ , *silver oxide*, from which the salts of silver can be derived; and  $\text{AgO}$ , *silver peroxide* (formed from silver and ozone).

**Silver oxide**,  $\text{Ag}_2\text{O}$ , is deposited as a dark brown amorphous precipitate when the solution of a silver salt is treated with caustic soda or baryta water free from carbonic acid. It is somewhat soluble in water (1 part in about 15,000 parts of water at room temperature); the solution probably contains the *silver hydroxide*, for it reacts alkaline and must therefore contain hydroxyl ions. By measuring the conductivity of its saturated aqueous solution it is found (see § 65) that only one-third of the molecules are ionized;  $\text{AgOH}$  is thus not so strong a base as the alkalis, but considerably stronger than ammonia. Moist silver oxide ( $\text{AgOH}$ ) absorbs carbon dioxide from the air and the silver salts react neutral, while the salts of most of the other heavy metals give an acid reaction because of a slight hydrolytic dissociation in aqueous solution. By heating to  $250^\circ$  silver oxide is broken up into its elements. It is reduced by hydrogen at as low a temperature as  $100^\circ$ . Ammonia water dissolves it readily, because a complex ion is formed.

**Silver chloride**,  $\text{AgCl}$ , is obtained by precipitating a silver solution with hydrochloric acid or a soluble chloride like sodium

chloride; it forms a characteristic "curdy" precipitate. It is almost insoluble in water, 1 part in 715,800  $H_2O$  at  $13.8^\circ$ .

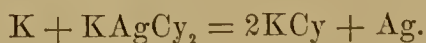
When a silver solution is added very carefully to a sodium ehloride solution (or to another ehloride), a point can be found when the liquid gives a cloudiness (due to  $AgCl$ ) with either solution. This must be attributed to the fact that the liquid is saturated with silver chloride and contains no other silver salt nor any other ehloride. In view of the very strong dilution of such a silver ehloride solution (see above) it may be assumed that the dissolved part is completely ionized. If silver or ehlorine ions are now introduced into the liquid, the ionization of the silver ehloride is diminished and  $AgCl$  moleeules are formed, which cannot remain in solution, since the solution is already saturated with them.

Silver chloride dissolves readily in ammonia, potassium cyanide and sodium thiosulphate, forming complex ions.

If a solution of silver chloride and ammonia is allowed to evaporate in the dark at room temperature, silver chloride crystallizes out in pretty, well-developed octahedrons.

**Silver bromide**,  $AgBr$ , is less soluble than the chloride and has a yellowish color. It dissolves with difficulty in ammonia but easily in thiosulphate. **Silver iodide**,  $AgI$ , is even less soluble than silver bromide at ordinary temperatures. It is insoluble in ammonia. It is yellow. At high temperatures these halides melt and on cooling form a horny mass, which can be cut with the knife (horn-silver, cf. § 245). **Silver fluoride**,  $AgF$ , is much more soluble in water than the three preceding halogen compounds.

**Potassium silver cyanide**,  $KAgCy_2$ , obtained on adding potassium cyanide to a silver solution, dissolves readily in water and is used in large quantities in electro-plating. When a current passes through it, potassium is deposited (primarily) at the cathode, while the anion  $AgCy_2$  wanders to the anode; however potassium precipitates silver from potassium silver cyanide:



Thus silver is deposited on the cathode while the anion  $AgCy_2$  takes up an atom of silver at the silver anode to form silver cyanide and again unites with potassium cyanide to form the double salt; if the anode is of platinum, cyanogen gas is set free from the anion,  $AgCy_2$ , and the anode becomes covered with silver cyanide, which soon interrupts the current.



All the silver salts, particularly the chloride, bromide and iodide, are sensitive to light, i.e. they are decomposed by light, especially by the violet and ultra-violet rays of the spectrum; as a result the halogen passes off and the color of the salt becomes first violet and then black. A blackened preparation of this sort can be re-whitened by chlorine- or bromine-water. The sensitiveness to light depends in large measure on the manner in which the silver halide is precipitated.

247. *Photography.* The property of silver chloride and silver bromide just mentioned forms the basis of photography. The process is essentially as follows: A glass plate is coated with a "sensitive film," i.e. a thin layer of silver chloride or bromide is spread over it. Formerly this was usually prepared by the photographers themselves from collodion (see Organic Chem. § 231) which contained a halogen salt, e.g.  $\text{CdI}_2$ , in solution. After the evaporation of the solvent a halide coating remained and by dipping the plates so prepared into a solution of silver nitrate, the silver halide was formed on them. These were the "wet plates"; now they are almost entirely superseded by the "dry plates."

The latter are prepared commercially on a large scale. They consist of a film of silver bromide in gelatine (less frequently in collodion) on a glass plate.

A sensitive plate of this sort is placed in the photographic apparatus, which is essentially a *camera obscura*, and the plate is there "exposed" to a light-image, which chemically affects the silver halide. It is very probable, that by the action of the light a subhalide is formed; the liberated bromine enters into combination with the gelatine or the collodion and is therefore unable to transform the subhalide into halide. As yet no picture can be seen on the plate; it must first be "developed." For the latter purpose the plate is immersed in a liquid containing a reducing substance. A typical developer is a solution of ferrous oxalate in an excess of potassium oxalate; various other organic compounds (amido-phenols, etc.) are at present frequently used. At those places on the plate where the light has struck, more or less silver (according to the intensity of the action of the light) is set free in the metallic form as a very thin coating, while the remaining silver halide is not affected by the developer. This halide must next be removed, else

it would be decomposed by the light and more silver liberated; therefore it is immersed in a solution of sodium thiosulphate ("hypo"). This operation is called "fixing" the image. Up to this time the plate must be kept from the light.

After the fixing we have a so-called negative, i.e. there remains on the glass plate a picture which is black in those places which were illuminated in the object and clear on those places which were dark. From this a positive impression is prepared by laying the negative on a paper coated with a sensitive film and exposing the whole to direct sunlight. Those places on the negative where silver was deposited let no light or very little through (according to their thickness), so that a positive image is now produced. Finally the positive image is also fixed, for which purpose a bath containing thiosulphate and a little gold chloride is used. The latter improves the color-tone of the photograph.

**Silver sulphate**,  $\text{Ag}_2\text{SO}_4$ , is obtained by dissolving silver in hot concentrated sulphuric acid. It is scarcely soluble in cold water.

**Silver nitrate**,  $\text{AgNO}_3$ , prepared by dissolving silver in nitric acid, crystallizes isomorphous with saltpetre in beautiful rhombic crystals. It is very soluble in water (1 part in 0.5 parts at room-temperature) and melts at  $218^\circ$ . In medicine it is frequently employed, especially as a caustic; it goes under the name of "lunar caustic." Indelible inks are also prepared from it.

**Silver nitrite**,  $\text{AgNO}_2$ , is formed as a yellowish precipitate on mixing an aqueous alkali nitrite solution and silver nitrate; it dissolves in boiling water and crystallizes on cooling in beautiful needles.

## GOLD.

**248.** This metal generally occurs *native*, being found in beds of quartz and alluvial deposits resulting from the decay of quartz rocks. Traces of gold have been detected in sea water. It occurs in Hungary, Siebenbuergen, the Ural and particularly in Australia, Transvaal and the western part of the United States and Canada. Recently large quantities have been discovered in Alaska (Klondike region). In Colorado considerable gold is obtained from tellurides (*sylvanite*, etc.).

The gold production of the world has more than doubled in the last

decade, amounting in 1900 to \$257,000,000, or about 387,000 kg. The principal gold-producing countries are :

United States.....	117,600 kg.
Australia.....	110,600
Canada . . . . .	42,000
Russia.....	34,000

But for political disturbances the Transvaal would take first rank. The chief causes of the rapid growth of the world's production have been the application of new processes in treating refractory ores and the development of new fields.

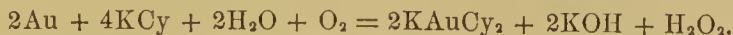
An ounce of gold is worth \$20.67; a kilogram \$664.60.

Inasmuch as the amount of gold contained in a cubic meter of ore or rock in the most profitable instances is only very small, it becomes the task of metallurgy to extract it from proportionately large quantities of rock.

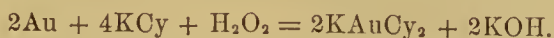
In the Transvaal this is accomplished as follows: The gold occurs there in so-called *reefs*, which are vertical veins in the quartz. These reefs are seldom more than one meter thick but extend for miles east and west; their depth is unknown. They are mined by blasting with dynamite; the large pieces are reduced to about the size of an egg in a heavy iron apparatus and then sent to the stamps, that move in a large trough through which plenty of water is kept running. The water carries off the fine auriferous slime, which is made to flow over amalgamated copper plates, that are somewhat inclined. The gold is retained by the mercury. After some time the plates are scraped off and the mercury removed by distillation, leaving the gold.

The extracted slime ("tailings") is treated again for gold, for which purpose the cyanide process of SIEMENS is employed.

By this process the tailings are allowed to stand for from one day to three weeks in contact with a 0.1 to 0.01% potassium cyanide solution. Under the influence of the oxygen of the air the gold dissolves in it, forming a double cyanide,  $\text{KAuCy}_2$  :



Hydrogen peroxide is also formed and serves to bring further amounts of gold into solution :



From this solution the gold is obtained by electrolysis between steel anodes and lead cathodes. At the anode Prussian blue (§ 308) is formed, which is treated for potassium cyanide; the gold is deposited at the cathode (§ 246). This gold is separated from the lead it contains by cupellation.

The following table shows the net results of the method described :

Yield.	1000 kg. ore, containing 18 g. gold.		Loss.
	Previous separation.		
	750 kg. ore with 17.046 g. gold.	250 kg. ore with 0.936 g.	0.936 g.
	Amalgamation process.		
9.385	9.385 g. or 55%	750 kg. ore with 7.679 g. gold.	
	Cyanide process.		
6.149	6.149 g.	1.530 g.	1.530 g.
15.534	recovered	lost	2.466
or 86.3%			or 13.7%

[Particularly in the United States two processes (chlorination and cyanide) are coming into general use for extracting gold from its ores without amalgamation. Both processes are especially applicable to low-grade and sulphurous ores, e.g. the tellurides of Colorado. In the *chlorination process* the ore is crushed and roasted and treated in revolving barrels with a mixture of bleaching-powder and sulphuric acid, after which the gold is precipitated with hydrogen sulphide and roasted. The *cyanide process* is much similar to that described above for treating the tailings, but zinc often serves as the precipitant instead of electrolysis.

*Placer* and *hydraulic mining* find application in newly discovered deposits but are much less common than *vein mining*. For the present status of gold metallurgy the student should consult a mining annual.—Tr.]

**249. Physical Properties.**—When pure, gold is reddish yellow, very soft (about like lead) and extremely malleable and ductile. The thinnest gold-leaf appears green in transmitted light. Sp. g. = 19.265 at 13°. It is a very good conductor of heat and electricity. At 1064° it melts to a greenish liquid.

*Chemical Properties.*—Gold is the typical representative of the precious metals; it is not attacked by acids and is dissolved only by chlorine water, aqua regia and potassium cyanide solution (see above). Its compounds are all very unstable; on warming they decompose, leaving the metal.

*Uses.*—About one-half the world's production of gold is used for industrial purposes. For these purposes the pure metal is too soft, however, and must be alloyed with copper or silver. The proportion of gold in the alloy is ordinarily expressed in *carats*; the pure metal is 24 carats; gold jewelry, etc., usually 14–18

carats, i.e. 24 parts of the alloy contain 14–18 parts of gold. The gold coins of the United States contain 1 part copper to 9 parts gold, those of England 1 part copper to 11 parts gold.

For purposes of *gold-plating* the same electrolytic processes are employed as for silver-plating.

#### Testing of Gold and Silver.

The oldest method of testing is by means of the *touchstone*, or “Lydian stone,” a black basalt. This stone must be dull black, unaffected by aqua regia and somewhat rough. The sample is rubbed on the surface of the stone so as to leave a bright streak of particles of the metal. This streak is then compared with that of a series of *touchneedles* of known composition.

Silver streaks are compared merely as to color. A skilled observer can usually estimate the proportion of silver to within 2.0–1.5%.

In the case of gold objects it must be known whether the metal contains copper, silver or both. Therefore the color of the streak is compared with that of touchneedles of the presumably corresponding alloy. The streaks are then moistened with a little acid consisting of 1 part HCl, 80 HNO<sub>3</sub> and 100 H<sub>2</sub>O. Alloys with 75% or more gold are not attacked by this mixture at ordinary temperatures. If the percentage is less, it is possible to detect differences of 1%. This method is decidedly crude and is usually employed only in confirming a supposed percentage. Where the metal is rich it is very deceptive; but gold of a quality such as is generally used for ornaments, etc. (ca.  $\frac{5883}{1000}$  fine) can be safely tested in this way.

A far more reliable test of the quality of gold is by cupellation. Part of the sample is fused with lead in a small muffle furnace in a small thick-walled, porous crucible (cupel) consisting of bone ash. At the high temperature of the furnace the lead and any copper present are oxidized and their oxides melt and are absorbed by the bone ash. As soon as they are completely taken up, the brilliant surface of the metal suddenly appears with splendid effect (*brightening* of gold). The residual drop of metal is an alloy of only gold and some silver. The latter is gotten rid of with boiling nitric acid, after the alloy left on the cupel has solidified and been hammered flat.

The proportion of silver in silverware is now determined exclusively in the wet way, by titration.

250. Gold forms two series of compounds analogous to the oxides Au<sub>2</sub>O, *aurous oxide*, and Au<sub>3</sub>O<sub>3</sub>, *auric oxide*.

### Aurous Compounds.

**Aurous oxide**,  $\text{Au}_2\text{O}$ , is obtained by treating the aurous chloride with dilute potassium hydroxide. It is a dark violet powder, which breaks up into its constituents at  $250^\circ$ .

**Aurous chloride**,  $\text{AuCl}$ , is produced by heating auric chloride to  $185^\circ$ . It is white and insoluble in water. When heated it splits up into its elements. On being warmed with water it yields  $2\text{Au}$  and  $\text{AuCl}_3$ .

**Aurous iodide** is formed (like cuprous iodide) on treating a solution of the chloride with potassium iodide.

The gold double cyanide,  $\text{KCy} \cdot \text{AuCy}$ , is prepared by dissolving auric oxide in potassium cyanide; it is used in gold-plating.

Of the oxy-salts of aurous oxide only a few double salts are known.

### Auric Compounds.

**Auric chloride**,  $\text{AuCl}_3$ , can be obtained by dissolving gold in aqua regia or by the action of chlorine on the metal. It forms a dark red crystalline mass, which deliquesces rapidly. On the evaporation of its solution it partially decomposes into chlorine and aurous chloride. By evaporating with hydrochloric acid long yellow needles are obtained, consisting of a compound  $\text{AuCl}_3 \cdot \text{HCl}$ , which can be regarded as *hydrochlor-auric acid*. Many salts of this acid are known to exist, e.g.  $\text{KCl} \cdot \text{AuCl}_3 + 2\frac{1}{2}\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cl} \cdot \text{AuCl}_3 + \text{H}_2\text{O}$ , as well as many salts of organic bases. These double salts give the ordinary tests, hence this acid either forms no complex ion  $\text{AuCl}_4'$  or is very unstable. Auric chloride is also soluble in alcohol and in ether.

**Auric oxide**,  $\text{Au}_2\text{O}_3$ , can be prepared by precipitating auric chloride with magnesia. The latter can be removed from the precipitate with concentrated nitric acid, the auric oxide remaining as a brown powder, which breaks up into its elements at  $250^\circ$ .

If the precipitate produced by magnesia is treated with dilute nitric acid, a reddish-yellow powder of the formula  $\text{AuO}_3\text{H}_3$  is obtained, which displays acid instead of basic properties. Salts of this auric acid are known, which are derived from the compound  $\text{Au}(\text{OH})_3 - \text{H}_2\text{O} = \text{AuO} \cdot \text{OH}$ . Potassium aurate, for ex-

ample, has the formula  $\text{KAuO}_2 + 3\text{H}_2\text{O}$  and crystallizes in yellow needles. Many other salts are also known; the above-mentioned precipitate with magnesia can be looked upon as the magnesium salt of auric acid,  $\text{Mg}(\text{AuO}_2)_2$ .

**Auric sulphide**,  $\text{Au}_2\text{S}_3$ , is precipitated from gold solutions by hydrogen sulphide. It is very dark brown and soluble in ammonium sulphide.

Gold is precipitated from its solutions in the metallic form by various reducing agents. Ferrous sulphate (§ 248) and oxalic acid serve very well for this purpose. Hydrogen peroxide precipitates gold quickly in alkaline solution. *Aqueous solutions of metallic gold* were obtained by BREDIG by comminuting gold wire under water by means of an electric arc. Colloidal solutions and a number of stages from such "pseudo-solutions" (which do not reveal any separate particles even when highly magnified) to real suspensions (see § 195) have also been prepared with other metals, notably silver, mercury and platinum, not only with the aid of reducing agents but also by comminution. They display various colorations according to the manner of preparation.

On adding stannous chloride to a gold solution under certain conditions a purple precipitate appears, which bears the name of *purple of Cassius*. It probably consists of a mixture of extremely finely divided gold and the hydrogel of stannic acid.

251. For many centuries the *alchemists* endeavored to produce gold from the baser metals. It is needless to say that their efforts were never rewarded. The chances of this hope being realized must at present be regarded as very slight, since gold is an element. Inasmuch, however, as our conception of an element is relative (§ 8), i.e. it depends on the extent of our mastery over natural forces, the impossibility of decomposing gold or synthesizing it from other elements is by no means absolutely established.

Although we now ascribe to every metal fixed, unalterable properties, it might well have seemed possible to the alchemists, with their more limited knowledge, that the properties of the metals could vary. None of the metals except gold occur pure in nature; they have to be extracted from oxides or sulphides, which frequently contain various impurities. The metals thus obtained had no definite properties; distinction was made between various sorts of lead, copper, etc. The mutability of the metals may be said to have been the first principle which observation taught; indeed, when a piece of metal is fused with small amounts of various other substances, its properties (color, etc.) really do change.

Moreover, at the time of the alchemists the present concept "element" was not yet established; this was first introduced by BOYLE (1627-1691). Before then, the doctrine of ARISTOTLE was very generally accepted, according to which all substances are made up of air, fire, earth and water. In order to produce gold it therefore seemed only necessary to deprive the baser metals of certain properties and substitute others. As to the metals themselves the idea was prevalent in alchemistic circles that mercury was the primordial substance and that it had undergone various changes. Before gold could be made from it it must be made refractory and of a yellow color. Not a few alchemists were convinced, moreover, that the success of the "great work" depended on the coöperation of a higher power.

### Summary of the Group.

252. The metals copper, silver and gold form a bridge from the difficultly fusible metals Ni, Pd, Pt (Group VIII) to the easily fusible, Zn, Cd, Hg (Group II); their melting-points are between those of the two groups. The following brief table summarizes the physical constants of these metals as well as those of the related elements, lithium and sodium:

	Li	Na	Cu	Ag	Au
Atomic weight.....	7.03	23.05	63.6	107.93	197.2
Specific gravity.....	0.59	0.97	8.94	10.5	19.33
Melting-point.....	180	97.6	1050	954	1200
Color.....	white	white	red	white	red

The analogy in the chemical properties is chiefly apparent in the *-ous* compounds. These have the type  $R_2O$  for the oxygen compounds and  $RX$  for the halides. The *-ous* halides of Cu, Ag and Au are all white and insoluble in water; they are isomorphous with sodium ehloride.

Farther, there are certain analogies in solubility. Lithium carbonate and hydroxide are less soluble than the corresponding sodium compounds; copper carbonate and hydroxide are insoluble, while the corresponding silver compounds dissolve to some extent in water. The sulphate of sodium (third horizontal series) crystallizes preferably with  $10H_2O$ , that of copper (fifth series) with  $5H_2O$ , while silver sulphate (seventh series) is anhydrous.

The oxygen compounds exhibit a gradual decrease in stability.



$\text{Li}_2\text{O}$  and  $\text{Na}_2\text{O}$  are unaffected by high temperatures, but  $\text{CuO}$  is transformed into  $\text{Cu}_2\text{O}$ , and the oxides of silver and gold break up even at comparatively low temperatures into their elements.

However, it must be admitted that the analogy between these elements is not so great as in other groups. Their difference in valence is especially striking and, moreover, there is little similarity in the properties of the higher stages of oxidation. This is one of the weak parts of the periodic system.

## BERYLLIUM AND MAGNESIUM.

### I. Beryllium (Glucinum).

**253.** This is one of the rarer elements. It occurs in the mineral *beryl*,  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 + 3(\text{BeO} \cdot \text{SiO}_2)$ ; that variety of beryl which is colored green by traces of a chromium compound is the gem called *emerald* or *smaragd*. *Chrysoberyl* has the composition  $\text{BeO} \cdot \text{Al}_2\text{O}_3$ .

Almost all the beryllium compounds are made from beryl. This is disintegrated by fusing with potassium carbonate. The fused mass, after cooling, is treated with sulphuric acid to precipitate the silica. Most of the aluminium is then removed by crystallization in the form of alum, as this is sparingly soluble in cold water, while beryllium sulphate remains in the mother liquor. The latter is then mixed with a hot solution of ammonium carbonate to precipitate aluminium and iron, beryllium still remaining in solution. After acidifying with hydrochloric acid, the beryllium is precipitated as hydroxide by ammonia.

The metal was obtained by heating  $\text{BeF}_2 \cdot 2\text{KF}$  with sodium. It is a malleable solid with the specific gravity 1.64. It does not decompose water, even at  $100^\circ$ . At ordinary temperatures it is permanent in the air. Hydrochloric and sulphuric acids dissolve it readily with the evolution of hydrogen; dilute nitric acid does not attack it so readily. Beryllium is also dissolved easily by caustic potash and soda with the evolution of hydrogen and the formation of salts having the formula  $\text{Be}(\text{OR})_2$ . The hydroxide thus behaves as a weak acid towards strong bases. These properties correspond to those of aluminium; in § 215 attention was already called to the analogy between these two elements. This analogy also characterizes their compounds, e.g., beryllium carbide yields pure methane with water, just like aluminium carbide (§ 178).

Only one oxide of beryllium is known,  $\text{BeO}$  (§ 215). It is a white powder, which after ignition is difficultly soluble in acids (like  $\text{Al}_2\text{O}_3$ ). It is obtained by heating the hydroxide,  $\text{Be}(\text{OH})_2$ , which is precipitated from solutions of the salts as a white gelatinous mass. The hydroxide (like  $\text{Al}(\text{OH})_3$ ) dissolves readily in alkalis. It is however distinguished from aluminium hydrate in two respects: it dissolves in ammonium carbonate

(see above) and is precipitated from the solution in caustic soda or potash by prolonged boiling.

**Beryllium sulphate**,  $\text{BeSO}_4$ , crystallizes with four or seven molecules of water, in the latter case being isomorphous with  $\text{MgSO}_4 \cdot 7 \text{ aq.}$  The double salt  $\text{BeSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  is (like alum) sparingly soluble in cold water. **Beryllium chloride**,  $\text{BeCl}_2$ , must be prepared from the oxide by heating with charcoal in a current of chlorine. Its vapor density corresponds to the formula  $\text{BeCl}_2$ . It crystallizes with  $4\text{H}_2\text{O}$ . **Beryllium carbonate** is soluble in water. It loses  $\text{CO}_2$  very easily.

The beryllium salts taste sweet, hence the name *glucinum* (or *glycinium*), which is common in France and America.

## II. Magnesium.

254. This element occurs as carbonate, silicate and chloride in considerable quantities. *Magnesite* is  $\text{MgCO}_3$ , *dolomite*  $\text{MgCa}(\text{CO}_3)_2$ . Among the silicates containing magnesium we have *talc*, *soapstone*,  $\text{H}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$ ; *serpentine (asbestos)*,  $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ ; *meerschauum*,  $\text{H}_4\text{Mg}_2\text{Si}_5\text{O}_{10}$ . It is found in smaller amounts in many other silicates, e.g. *hornblende (asbestos)*, *augite*, *tourmaline*. Other salts found in nature are *carnallite*,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ , *kieserite*,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , and *kainite*,  $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$  (*Stassfurt Abraham salts*). Upon the weathering of the silicates the magnesium goes into the soil, whence it is absorbed by the plants (to which this element is invaluable) and finally taken into the animal body.

The metal is manufactured on a large scale, since it is employed for illumination in photography, pyrotechnics, etc., on account of its intense light (*flash-light*). At present it is prepared mainly by the electrolysis of fused magnesium chloride or carnallite in a cast-steel crucible, which serves as cathode; gas carbon is used for the anode. It is also obtained by heating  $\text{MgCl}_2 \cdot \text{NaCl}$  with sodium. It is silvery white and has a high lustre. Sp. g. = 1.75. It is malleable and ductile and comes on the market in the form of wire or ribbon as well as powder, but the ribbon frequently contains zinc. It melts at  $800^\circ$  and distills at red-heat. It is quite permanent in the air, since it soon becomes coated with a thin cohesive film of the oxide; at an elevated temperature it burns to magnesia,  $\text{MgO}$ . When it is heated red hot in a limited supply of air, a large part is converted in nitride  $\text{Mg}_3\text{N}_2$ , a yellowish green substance. Boiling water decomposes it slowly

with the evolution of hydrogen. It dissolves readily in acids but is unaffected by alkalis. It is a powerful reducing agent, reducing silica (§ 190), for example; moreover, when ignited, it continues to burn in water vapor.

**Magnesium oxide**,  $MgO$ , *magnesia*, is the only oxide of magnesium known. It results from the combustion of the metal or from heating the hydroxide or carbonate. It is a white, very light powder, which is employed in medicine under the name *magnesia usta*. With water it forms the hydrate  $Mg(OH)_2$ .

**Magnesium hydroxide**,  $Mg(OH)_2$ , is precipitated from solutions of magnesium salts by alkalis. It is slightly soluble in water and turns red litmus blue; however in an excess of alkali its ionization is so diminished that it becomes practically insoluble. It is only a weak base, but is strong enough to absorb carbon dioxide from the air. It dissolves readily in an aqueous solution containing ammonium salts. According to OSTWALD, this is to be explained as follows: The solution of an ammonium salt contains a large quantity of  $NH_4$ -ions. When a substance is introduced into the solution, which gives off  $OH$ -ions, as does magnesium hydroxide, these  $NH_4$ -ions unite with  $OH$ -ions to form  $NH_4OH$ , or rather  $NH_3 + H_2O$ . As a result of this reaction  $OH$ -ions disappear. In order to restore the equilibrium between the undissolved magnesium hydroxide and the solution, more of this hydroxide must go in solution, but again the freshly formed  $OH$ -ions are taken up by the  $NH_4$ -ions. If sufficient of the latter are present, this process will go on till all the magnesium hydroxide has entered into solution. It now becomes clear, why on the other hand, the solution of a magnesium salt is not precipitated by ammonia in the presence of a sufficient quantity of ammonium salt.

#### MAGNESIUM SALTS.

**255. Magnesium chloride**,  $MgCl_2$ , crystallizes with six molecules of water and is very hygroscopic. The deliquescence of common salt is due to the magnesium salt it usually contains. For the rôle of this salt in the Solvay process *cf.* § 226, 2. On evaporating the aqueous solution  $Mg \begin{smallmatrix} OH \\ Cl \end{smallmatrix}$  and  $HCl$  are formed; sea-water cannot be used in boilers because of the magnesium salt it contains, for the hydrochloric acid set free attacks the iron too strongly. Many double salts of magnesium chloride are known.

It can be obtained anhydrous by heating  $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6 \text{ aq}$ , when it forms a laminar-crystalline mass, which melts at  $708^\circ$  and distills without decomposition at bright red heat.

**Magnesium sulphate**,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , *Epsom salt*, finds use in medicine. It is very soluble in water. It loses 6 mols.  $\text{H}_2\text{O}$  at  $150^\circ$ , and the seventh above  $200^\circ$ . In this respect it behaves like other sulphates, e.g.  $\text{ZnSO}_4 \cdot 7 \text{ aq}$ ,  $\text{FeSO}_4 \cdot 7 \text{ aq}$ , as well as those of nickel and cobalt, which are moreover isomorphous with it. A further analogy between these sulphates appears in the fact that with sulphate of potassium or ammonium they form double salts of the same type,  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6 \text{ aq}$ , which are also isomorphous.

**Magnesium ammonium phosphate**,  $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{ aq}$ , serves for the precipitation of magnesium as well as that of phosphoric acid. It is not wholly insoluble in water, but does not dissolve in ammonia, the reason for which conduct is again to be sought in the reduction of the ionization. Completely analogous to this compound is the corresponding arsenate,  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ .

**Magnesium carbonate**.—From solutions of magnesium salts soda precipitates a basic carbonate,  $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 4 \text{ aq}$ . The carbon dioxide liberated holds part of the magnesium in solution as acid carbonate. This precipitate is known as *magnesia alba*. The neutral carbonate can be prepared from it by suspending *magnesia alba* in water, passing in carbon dioxide and allowing to stand; in time  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  crystallizes out, which is, however, readily split up hydrolytically by water, forming again basic carbonate.

## CALCIUM, STRONTIUM AND BARIUM.

### I. Calcium.

256. This element is one of the ten principal constituents of the earth's crust (§ 8). Particularly the carbonate is found in large quantities in nature, *limestone*, *calcite*, *aragonite*, *marble* and *chalk*, all being forms of it. An earthy deposit containing a certain amount of calcium carbonate is termed *marl*. Calcium silicates and especially calcium double salts constitute the major portion of the siliceous rocks. There are also extensive beds of calcium phosphate, *phosphorite*, *apatite*, etc., particularly in Spain and Florida. Calcium occurs as sulphate in the form of *gypsum*.

and *alabaster*. Moreover, in the animal kingdom large quantities of this element are found. The skeletons of vertebrates are chiefly phosphate and carbonate of calcium; the shells of mollusks consist of calcium carbonate, as do also egg shells. As for the plants, lime is one of their invaluable inorganic constituents.

Metallic calcium can be obtained either by electrolysis of fused anhydrous calcium iodide or by decomposition of the same salt with sodium at red-heat. If an excess (three times the theoretical amount) of sodium is taken in the latter operation, the calcium dissolves in the molten sodium and crystallizes out on cooling. The sodium can be removed with absolute alcohol, which acts on calcium only slightly at ordinary temperatures. Calcium is a silvery-white metal, which melts at  $760^{\circ}$ ; it is soft enough to cut and is malleable, but less so than potassium and sodium; it has a crystalline fracture. Sp. g. = 1.78-1.87. It is relatively little affected by oxygen, chlorine, bromine and iodine, all of which react with the metal only at a higher temperature than the ordinary one. In a current of air calcium unites with both oxygen and nitrogen (§ 110).

#### OXIDES AND HYDROXIDES OF CALCIUM.

257. Calcium oxide,  $\text{CaO}$ , (quick-lime, unslaked lime) is prepared commercially by "burning" limestone or mollusk shells. The limestone is mixed with coal and the latter is set on fire; the heat of the burning coal dissociates the carbonate of lime into calcium oxide and carbon dioxide. The kilns are usually constructed in such a way that the burned lime can be drawn out at the bottom while the mixture of fuel and limestone is fed in at the top, so that the process is continuous. In the United States "long-flame" periodic kilns are generally used because they are simpler and fuel is inexpensive.

Calcium oxide is a white amorphous powder, which requires the temperature of the electric furnace for fusion (§ 176). On being heated strongly with an oxy-hydrogen flame it emits an intense white light (§ 13). It absorbs water and carbon dioxide from the air; as a result the chunks of lime, which are hard and solid when they come from the kiln, gradually crumble to fine powder.

Calcium hydroxide,  $\text{Ca(OH)}_2$ , (slaked lime) is obtained by

“slaking” quick-lime with water. Its formation is attended by the evolution of much heat. It is only sparingly soluble in water (forming *lime-water*), but more soluble in cold water than in warm. The solubility is, however, sufficient to make the precipitation of this hydroxide by ammonium hydroxide impossible, for the concentration of the hydroxyl ions of the latter is too small together with that of the calcium ions present to reach the value of the solubility product of calcium hydroxide. At red-heat it is recon-verted into the oxide.

*Mortar*.—Calcium hydroxide is used in masonry. For this purpose it is mixed with water and sand so that it forms a thick paste, called *m o r t a r*, which is thrown in between the stones. After some time the mass becomes as hard as stone; this is due to the conversion of the hydroxide into the carbonate by the carbon dioxide of the air. The sand makes the mass porous so that the process of hardening extends inward; the older the wall, the harder the mortar. The formation of calcium silicate appears to play only a minor rôle in this process.

If the lime contains more or less magnesia, it is difficult to slack; it is therefore less adapted to masonry purposes and is called “poor,” or “lean,” in contrast with the pure, easily slaked “fat” lime.

*Cement* contains, besides lime (50–60%), principally silica (ca. 24%) and alumina (ca. 8%). It is made by burning a mixture of limestone, clay and sand. In some places, e.g. Brohlthal in the Rhine region, such a mixture occurs as “tuffstone,” which yields cement directly on burning. Cement after being mixed with water sets very firmly in a short time; this is due, in all probability, to the fact that on treating it with water calcium aluminate is dissolved and the solution deposits a hydrous aluminate after some time, which is much less soluble and causes the setting of the cement. At the same time insoluble calcium aluminium silicates are formed.

Calcium peroxide,  $\text{CaO}_2 + 8\text{H}_2\text{O}$ , is deposited when lime-water is treated with hydrogen peroxide solution. It gives up oxygen on heating.

#### SALTS OF CALCIUM.

258. Calcium chloride,  $\text{CaCl}_2$ , is obtained by dissolving the hydroxide or carbonate in hydrochloric acid. It can crystallize

with various amounts of water. The hydrate  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  forms large crystals. Calcium chloride is very hygroscopic and is therefore frequently used to dry gases or to absorb water dissolved in organic liquids (ether, carbon bisulphide, etc.). It melts at  $719^\circ$ . It unites with ammonia to form  $\text{CaCl}_2 \cdot 8\text{NH}_3$ ; hence it cannot be used to dry this gas.

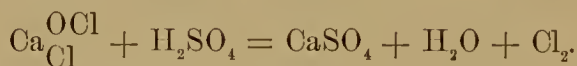
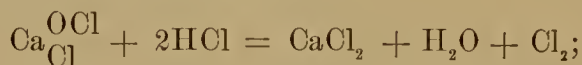
When crystallized calcium chloride is mixed with ice the temperature falls very considerably, even reaching  $-48.5^\circ$ . Such a mixture is called a *cooling* or *freezing mixture* and is often employed for producing low temperatures. Besides calcium chloride and ice, many other such mixtures are known; the one most frequently used is that of common salt and ice, which can give a temperature of  $-21^\circ$ . Ice is not absolutely necessary; for instance, if solid ammonium nitrate is added to its own weight of water, a temperature of  $-15.5^\circ$  can be produced.

In order to understand why such mixtures become so cold, we must recall § 237. Suppose that ice is introduced into a saturated salt solution of  $0^\circ$ , solid salt being present at the bottom so that the liquid remains saturated. The system solution + ice is not in a state of equilibrium at  $0^\circ$ , for the salt solution has a freezing-point much lower than  $0^\circ$ . It cannot therefore continue in this state; but if it is to be in equilibrium with ice as solid phase, the temperature must sink, and this is only possible as the ice melts, by which process heat is changed into a latent condition. If enough ice is present, it can, by melting, continue to withdraw free heat from the system till the cryohydric point is reached; for only from that point can ice and salt exist permanently side by side. It follows therefore that the cryohydric is the lowest temperature that can be reached by the mixture. In § 237 it was also shown that there is no essential difference between the two components of a solution; this is also made plain by considering cooling mixtures containing no ice. For instance, when ammonium nitrate is added to water, the solution has a freezing-point much lower than  $0^\circ$ . Here it is the great absorption of heat in dissolving the salt, that causes the fall of temperature necessary to establish the equilibrium. If this fall is to be considerable, the solubility of the salt must of course be great. In this case also the cryohydric point is the lowest temperature that can be reached by the mixture.

**Chloride of lime** is a name given to a product obtained by saturating slaked lime with chlorine at ordinary temperatures. Just what compound is formed here is not yet definitely known although the matter has been frequently investigated. There is, however, much evidence in favor of the formula  $\text{Ca} < \begin{matrix} \text{OCl} \\ \text{Cl} \end{matrix}$ , according to which it is a mixed salt of hydrochloric and hypochlorous

acids. At any rate this is more probable than the supposition that chloride of lime is a mixture of calcium hypochlorite and calcium chloride (§ 56), for it is not possible to extract any chloride of calcium from it with alcohol, although this salt is very soluble in alcohol, and almost all the chlorine is expelled by a current of carbon dioxide.

Chloride of lime is employed in large quantities for bleaching and disinfecting (*bleaching-powder*). It is an incoherent white powder with the odor of chlorine (on account of decomposition by the carbon dioxide of the air). When treated with hydrochloric or other acids it yields chlorine:



A solution of chloride of lime, when mixed with a cobalt salt and warmed, evolves oxygen. This reaction can be regarded as primarily an oxidation of CoO to Co<sub>2</sub>O<sub>3</sub>, the latter then yielding oxygen with chloride of lime and forming CoO anew. The cobaltous oxide would thus be a catalyzer.

**Calcium fluoride**, CaF<sub>2</sub>, occurs in nature as *fluor spar* or *fluorite*, forming cubes, which are often fluorescent. It is insoluble in water. It fuses at red-heat and is frequently employed as a flux in metallurgical processes. It can be obtained artificially by treating a solution of calcium chloride with sodium fluoride, NaF.

**Calcium sulphate**, CaSO<sub>4</sub>·2H<sub>2</sub>O, occurs in nature as *gypsum* (§ 256). It is only slightly soluble in water. At 110° it loses water of crystallization; the resulting powder takes up water again at ordinary temperatures. On being stirred up with water into the form of paste it soon becomes solid; this is the basis of its use (as "plaster of Paris") in making casts.

In case the gypsum has been heated too high in dehydrating, it unites with water very slowly. It is said to be "dead-burnt" and has in fact passed over into another (β) modification, which, however, changes slowly back into the ordinary (α) form. All burned gypsum contains a little of the β-modification. On being mixed with water the α-modification takes up water first; the gradual absorption of water by the other modification causes the plaster to increase in firmness for some time afterward.

The reason why gypsum "sets" on taking up water, instead of forming



a loose lot of crystals, is attributed by LE CHATELIER to the fact that a gypsum solution which is saturated with respect to anhydrous salt (the latter being therefore the solid phase), contains more salt than when the hydrous salt is the solid phase. Therefore in a paste of gypsum the anhydrous calcium sulphate continues to dissolve in the solution which is supersaturated in respect to hydrous crystals; as a result the latter keep on growing and are cemented together by the freshly deposited material.

**Calcium nitrate**,  $\text{Ca}(\text{NO}_3)_2$ , results from the decay of nitrogenous organic substances in the presence of lime. It crystallizes with four molecules of water. The anhydrous salt deliquesces in the air and dissolves readily in alcohol. It is converted into salt-petre by potash or potassium chloride (§ 229).

**Calcium phosphates.**—The *tertiary* salt,  $\text{Ca}_3(\text{PO}_4)_2$ , is insoluble in water, as is also the *secondary* salt,  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$ . The *primary* salt,  $\text{CaH}_4(\text{PO}_4)_2$ , however, is readily soluble in water; it is employed in large quantities as an artificial fertilizer, under the name of **s u p e r p h o s p h a t e**.

The manufacture of superphosphate is effected by thoroughly mixing ground phosphorite (or bone meal) in a cast-iron mixer with chamber acid according to the proportions of the equation



The mass, which is at first semi-solid, soon becomes solid since the calcium sulphate that is formed takes up the water contained in the chamber acid to form crystals.

When superphosphate is mixed with soil the primary calcium sulphate goes into solution and, since every soil contains lime, it is forthwith reconverted into insoluble secondary or tertiary phosphate. Apparently nothing has been gained toward "making the phosphoric acid soluble." However the phosphate is now diffused widely in the soil and is therefore much more accessible to the roots of the plants than if the soil had been mixed with tertiary phosphate only.

**259. Calcium carbonate**,  $\text{CaCO}_3$ , is dimorphous, occurring rhombohedral as *calcite* and rhombic as *aragonite*. When the solution of a calcium salt is treated with soda, calcium carbonate is deposited, the precipitation being at first amorphous and very voluminous; after a short time, however, it turns to a finely crystalline powder. It is very slightly soluble in water, but more extensively so in water containing carbonic acid, since the acid calcium carbonate is then formed. The latter decomposes when the solution is boiled, carbon dioxide escaping and crystalline neutral carbonate being deposited.

*Hardness of Water.*—Almost every river- or spring-water holds more or less lime in solution. The lime is present as sulphate or as acid carbonate. Such a water forms but little, if any, lather with soap; the fatty acids of the soap form white insoluble salts with the lime, wherefore water containing much lime is not good for washing. Such a water is termed *hard* in contrast with a water that is free or nearly free from lime, which is called *soft*. If the hardness is due to acid carbonate (also called “bicarbonate” of lime), it disappears on protracted boiling, calcium carbonate being precipitated. In such a case we speak of *temporary hardness*. In metallic boilers and similar vessels the carbonate of lime that is deposited adheres firmly to the sides (“boiler scale”). If the hardness of a water is due to gypsum, which is only partially removed by heating (§ 236), it is spoken of as *permanent hardness*.

When heated, calcium carbonate breaks up into lime and carbon dioxide. We have here a case of complete heterogeneous equilibrium (§ 71), for the substances are  $\text{CaO}$  and  $\text{CO}_2$  and the phases  $\text{CaO}$ ,  $\text{CaCO}_3$  and  $\text{CO}_2$ . This is confirmed by experiments, which show that the concentration of the gaseous phase (the dissociation tension) at a definite temperature is constant and therefore independent of the amount of each phase. Complete decomposition into lime and carbon dioxide can only occur, therefore, when the gaseous phase is removed (as in lime-burning, § 257) or when its tension is kept below the dissociation tension. On the other hand, if the tension of the carbon dioxide is greater than the dissociation tension, calcium carbonate cannot decompose. Under these circumstances it is possible to fuse calcium carbonate; on solidification it assumes a crystalline structure and becomes *marble*.

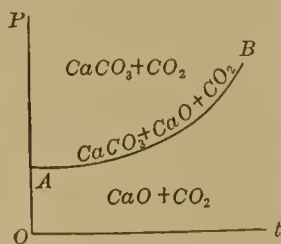


FIG. 70.

In the adjoining Fig. 70, let  $AB$  represent the dissociation curve of calcium carbonate in a coordinate system  $Pt$ . Only along this curve are the three phases in equilibrium with each other; under any other conditions one of the phases disappears and we enter either the region of the phases  $\text{CaO} + \text{CO}_2$  or that of  $\text{CaCO}_3 + \text{CO}_2$ .

**Calcium oxalate**  $\text{CaC}_2\text{O}_4 + 2\text{H}_2\text{O}$ , is deposited when ammonium oxalate.

is added to the solution of a calcium salt. The precipitate is insoluble in acetic acid, but soluble in mineral acids. This is a good illustration of the statement in § 146 that those salts which are insoluble in water dissolve only in acids that are stronger than the acid of the salt. According to their conductivities acetic acid is less ionized and the strong mineral acids more ionized, than oxalic acid. The addition of the slightly dissociated acetic acid causes only a partial combination of the H-ions and  $C_2O_4$ -ions (anions of oxalic acid) so that only very little calcium oxalate has to dissolve before the value of the solubility product is again reached. The addition of a strong mineral acid, however, causes the H- and  $C_2O_4$ -ions to unite to such an extent that the solubility product of calcium oxalate can no longer be reached and the latter must therefore dissolve completely.

## GLASS.

**260. Calcium silicate** is chiefly important because it is a constituent of almost all sorts of glass.

*Glass* is a mixture of silicates of the alkalies with calcium or lead silicate. The alkali silicates are soluble in water, amorphous and easily fusible. The calcium silicates, however, are insoluble, very hard to fuse and frequently crystallized. By fusing both together an insoluble amorphous transparent mass of moderate fusibility is obtained, which is glass. It is prepared by fusing a mixture of clean sand, lime and soda in refractory crucibles.

The properties of glass depend primarily on the quality of the materials and secondarily on the proportions used. By varying these two conditions it is easy to obtain grades of glass varying widely in fusibility, hardness, lustre, refractive power, etc. There are very many different sorts in use. Some of the most important are the following:

**Soda glass** (*window glass*) is a soda-lime silicate. It is readily fusible and is used for most purposes of the household.

**Potash glass** (*crown glass, Bohemian glass*) consists of a silicate of potassium and calcium. It is very difficult to fuse and is therefore extensively used for chemical purposes (combustion tubes, etc.).

**Lead glass** (*flint glass*) is a silicate of potassium and lead. It is softer, more easily fusible and highly refractive and takes on a beautiful lustre when polished. It is therefore used for optical instruments and fancy glassware ("cut glass").

Besides the substances mentioned many others are used in glass.

factories to impart particular properties to the glass. The addition of boric acid or the partial replacement of lead with thallium gives lead glass a still higher refractive index. An admixture of alumina,  $\text{Al}_2\text{O}_3$ , prevents or hinders chemical utensils of glass from becoming brittle and allows the replacement of part of the alkali by lime. Certain metallic oxides form colored silicates and are therefore mixed in with the furnace charge to color the glass (cobalt, blue; chromium or copper, green; uranium, yellow-green fluorescent; etc.). The addition of bone-ash,  $\text{Ca}_3(\text{PO}_4)_2$ , or tin oxide gives a milky-white opaque glass. In the table below are given the results of some analyses of different kinds of glass, affording an idea of their percentage composition:

	$\text{SiO}_2$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{PbO}$	$\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$
Window glass.....	70	.....	13	13	.....	1
Bottle glass. ....	60	.....	3	25	.....	7
Crown glass.....	73	11.5	3	11	.....	1
Flint glass.....	50	11	.....	.....	38	0.5

Water has in general very little effect on glass, nevertheless it attacks it somewhat. Old window-panes have a peculiar iridescence, due to surface weathering. As it is very important in exact analyses to know how much glass can be dissolved from the utensils, careful investigations have been carried out, the results indicating the following: When the glass is new a relatively large amount goes into solution; this amount gradually decreases in the course of a few weeks to a minimum. At the first the alkali in particular is dissolved from the surface and the resulting solution then acts as a solvent for the silicic acid. To prepare glass vessels so that they are almost wholly unaffected by water they are subjected to a jet of steam for a quarter of an hour or left for several weeks full of water, the water being renewed occasionally. Thus there is formed on the surface a thin layer, rich in silica and lime, which protects the inner portion from the action of the water.

The dissolving action of water on the alkali of glass can be readily shown by agitating finely powdered glass in water. The liquid at once turns phenolphthalein bright red.

Glass is a typical amorphous substance. Such substances are often defined as liquids with a very high internal friction and the behavior of molten glass on cooling is an excellent illustration of this definition. At high temperatures molten glass is a thin liquid; if the temperature is allowed to sink, the consistency of the glass becomes tougher so that between the wholly liquid and the wholly "solid" state there is a continuous series of half-liquid states. As it is thus impossible to fix a limit to the applicability of the laws for solutions, e.g. that of diffusion, it seems rational to consider the "solid" amorphous state as a liquid, in contradistinction to the crystalline state, which latter is truly solid, having very different properties than liquids.

**Calcium sulphide**,  $\text{CaS}$ , is formed by calcining gypsum with charcoal. On treating with water calcium hydrosulphide,  $\text{Ca}(\text{SH})_2$ , is formed, whose aqueous solution decomposes on boiling. The sulphide (like that of barium and that of strontium) has the property of emitting light in the dark, if it has been previously exposed to sunlight, but seems only to show this phenomenon when it contains traces of other elements, such as vanadium or bismuth.

## II. Strontium.

**261.** This is one of the less widely diffused elements. The principal strontium minerals are *strontianite*,  $\text{SrCO}_3$ , and *celestite*,  $\text{SrSO}_4$ . Its compounds are very analogous to those of calcium.

The metal has been obtained by the electrolysis of fused strontium chloride. Its specific gravity is 2.5. In its properties it corresponds to calcium throughout.

**Strontium oxide**,  $\text{SrO}$ , is formed on igniting the hydrate or carbonate. The temperature for the complete dissociation of the latter is higher than that for the corresponding calcium compound. The **hydroxide**,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , is more soluble in water than calcium hydroxide. The **chloride**,  $\text{SrCl}_2 + 6\text{H}_2\text{O}$ , is also hygroscopic. It is soluble in alcohol and can, with the aid of the latter, be easily separated from barium chloride, which is insoluble in alcohol. **Strontium sulphate** is much less soluble than calcium sulphate; at  $16.1^\circ$  1 part  $\text{SrSO}_4$  dissolves in 10070 parts  $\text{H}_2\text{O}$  ( $\text{CaSO}_4$ , 1 part in 543 at  $15.2^\circ$ ). In a mixture of alcohol and water it dis-

solves to an extremely small degree. **Strontium nitrate**,  $\text{Sr}(\text{NO}_3)_2$ , is insoluble in alcohol; this forms the basis of separating it from **calcium nitrate**, which dissolves in alcohol.

Strontium salts are used in pyrotechnics because of the beautiful crimson color they impart to a flame.

### III. Barium.

**262.** This element occurs combined as *barite*, or *heavy spar*,  $\text{BaSO}_4$ , and as *witherite*,  $\text{BaCO}_3$ , in considerable quantities. In preparing the other barium salts it is merely necessary to dissolve the latter mineral in the proper acid. The barite must first be ignited with charcoal and so reduced, whereupon the resulting barium sulphide is decomposed with acids.

The metal is, in this case also, obtained by the electrolysis of the fused chloride. Another method is to treat a hot barium chloride solution with sodium amalgam, forming barium amalgam; on distilling off the mercury in a current of hydrogen, the barium is left, although not entirely free from mercury. It decomposes water vigorously even at ordinary temperatures. Sp. g. = 3.75.

**Barium oxide**,  $\text{BaO}$ , is obtained by igniting the nitrate or hydroxide at a high temperature. It unites very readily with water to form the **hydroxide**,  $\text{Ba}(\text{OH})_2$ , which is rather soluble in water (yielding *baryta-water*), and crystallizes from the hot solution on cooling in pretty laminae, which contain eight molecules of water.

**Barium peroxide**,  $\text{BaO}_2$ , forms on heating the oxide in a current of oxygen or air. When it is introduced into dilute sulphuric acid, barium sulphate is precipitated and hydrogen peroxide left in solution. If baryta-water is again added,  $\text{BaO}_2 + 8\text{H}_2\text{O}$  crystallizes out.

**Barium chloride**,  $\text{BaCl}_2 + 2\text{H}_2\text{O}$ , is not hygroscopic like  $\text{SrCl}_2$  and  $\text{CaCl}_2$ . The nitrate crystallizes anhydrous.

**Barium sulphate**,  $\text{BaSO}_4$ , is characterized by an exceedingly small solubility in water and acids; at  $18.4^\circ$  1 part dissolves in 429,700 parts  $\text{H}_2\text{O}$ . It is used as a filler and as a pigment under the name of "permanent white," or *blanc fixe*. **Barium carbonate** yields carbon dioxide only at very high temperatures, prolonged heating at  $1450^\circ$  being required for complete decomposition.

### Summary of the Group of the Alkaline Earths.

The following small table summarizes the physical properties of the elements of this group:

	Be	Mg	Ca	Sr	Ba
Atomic weight . . . . .	9.1	24.36	40	87.6	137.4
Specific gravity . . . . .	1.64	1.75	1.58	2.5	3.75
Atomic volume . . . . .	5.6	13.8	25.2	34.9	36.5
Color . . . . .	white	white	white	.....	.....

As to the specific gravity we observe that only in the cases of Ca, Sr and Ba is a steady increase noticeable.

In respect to the chemical properties, it has already been remarked that these elements act only as bivalent; all compounds of the group therefore have the same formula type. In the solubility of the sulphates a gradual decrease is to be observed with rising atomic weight.

Just as in the first group three elements, K, Rb, Cs, exhibit a particular kinship, so here calcium, strontium and barium are closely related in their properties, while the two other members of the group are unlike them in many respects. Beryllium displays analogy with aluminium in certain points just as lithium does with magnesium.

### SPECTRAL ANALYSIS.

263. If the light from an ordinary gas-flame or the WELSBACH incandescent light is broken up by a prism, there is projected a continuous series of perfectly blended colors from red through yellow, green and blue to violet. This phenomenon is called a **spectrum**, and, since it is unbroken, a **continuous spectrum**. We have previously remarked that the luminosity of a gas-flame is due to incandescent solid particles of carbon. It has been found to be a general rule that incandescent solids give a continuous spectrum.

With incandescent gases it is different. If, for instance, we split up the light from a Bunsen flame, in which salts of sodium, calcium or other metals are volatilized, we see only a few narrow bands of light in certain places, the rest of the spectrum

being dark. This is termed a line spectrum. Every element has its own peculiar *spectrum lines*. If the spectrum of the incandescent vapors of a mixture of elements is carefully examined, it is found to contain all the characteristic lines of each element. Since it is only necessary to volatilize extremely small amounts of substances in order to show their lines, it is readily seen how important the spectrum-analytical methods introduced by BUNSEN and KIRCHHOFF must be.

For the examination of spectra a number of instruments have been constructed, varying according to the particular object in view. For chemical analysis the apparatus of VOGEL or that of JOHN BROWNING is now very generally used. It is a small direct-vision spectroscope which gives a very bright spectrum and has a sufficient dispersion. At the end *B* (see Fig. 71) is the slit which

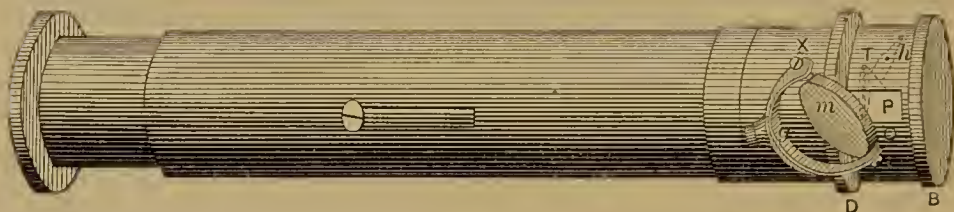


FIG. 71.

can be made narrower or wider by turning the rim *D*. The small mirror *m* serves to throw light through the hole *P* on to an auxiliary prism, in order to compare the spectrum of the light which is to be analyzed with that of a known source. At the left end is the ocular through which the spectrum is seen. For further information text-books on physics should be consulted.

In order to examine the spectra of metals it is necessary to convert the latter into the form of vapor at a high temperature. There are different ways of doing this. One is to introduce salts of the metals into a colorless flame by means of a platinum wire. The heat dissociates halogen salts and in the case of oxy-salts converts them into oxides, which are reduced to the metallic condition by the hot gases of the flame. This method is very satisfactory when there is plenty of material. If that is not the case a *flame spectrum* of this sort is not so good as a *spark spectrum*, for with the latter it is possible to detect with accuracy



extremely small amounts of a substance. Other advantages of the spark spectrum are its greater light intensity, the greater convenience in execution, and the like. Moreover at the high temperature of the sparks most elements exhibit spectra which cannot be obtained with the gas-flame.

A spark spectrum can be obtained in a very simple manner. thus: Into the bottom of a little glass cup (*n*, Fig. 72), about 15 mm. wide is fused a platinum wire, which ends in a tube *g* containing mercury and is thus connected with the negative pole of an inductor; it is incased in a conical capillary tube *x*, that projects about 0.5 mm. beyond the wire. At the opposite end is the positive electrode in the form of a platinum wire, which, with the exception of the short end *d*, is fused into a glass tube; the latter is fitted into the cork *a*. If some of the salt solution is poured into the cup about half way up the negative electrode, the liquid is drawn up to the end of *x* by capillarity and every spark volatilizes a tiny portion. In this way there is no loss of material and the sparks are very uniform, so that the observation of the spectrum can be continued at length.

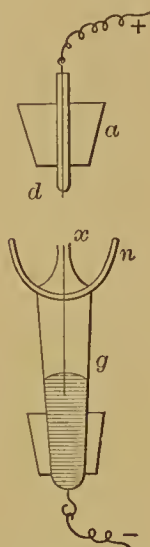


FIG. 72.

For the study of the spectra of substances which are gaseous at ordinary temperatures the PLÜCKER-HITTORF (GEISSLER) tubes are used (Fig. 73). The gases are sealed up



FIG. 73.

in them in a very dilute condition. On connecting one of these with the poles of an induction coil, the whole tube is illuminated, most intensely in the narrow portion. This part is placed in front of the slit of the spectroscope.

Some substances have the property of absorbing certain colors and transmitting others. If the solution of such a substance is placed before the slit of a spectroscope and the light of a continuous spectrum allowed to pass through it, dark bands or lines are

observed in the spectrum. A number of substances have very characteristic absorption spectra.

264. The spectroscope is one of the most delicate means we have of detecting many substances. This is readily seen on considering how small an amount of the substance under examination is volatilized by the sparks. We arrive at numbers like  $0.3 \times 10^{-6}$  mg. sodium, for instance, as the least amount that can be detected. It has thus been possible to discover elements which occur only in company with large amounts of others and would therefore have been very difficult to find in the ordinary way. BUNSEN and KIRCHHOFF themselves found cæsium and rubidium in this way in Dürkheim mineral water. In order to obtain these elements from it in the form of chlorides, it was necessary to evaporate 44,000 kg. water, which yielded 16.5 g. of a mixture of the chlorides. Other very rare elements which were discovered by spectral analysis are thallium, indium, gallium, ytterbium and scandium.

The spectra of the elements differ widely in appearance; some, e.g. those of sodium, thallium and indium display only one distinct line (see plate); others, such as those of barium, strontium, calcium and especially iron, are very complex and consist of very numerous lines of varying intensity. Among these there are some which are easily recognized and have a characteristic position. Thus, for example, rubidium and cæsium are most readily detected in spectroscopic work by means of their closely adjacent blue lines.

265. Attempts have been repeatedly made to find some connection between the positions of the different spectral lines of an element or between those of the different elements of the same group.

LECOQ DE BOISBAUDRAN has called attention to the fact that the principal lines of the spectra of the alkalis and alkaline earth move towards the red end as the atomic weight increases. The blue lines of potassium are close to the ultra-violet portion; in rubidium and cæsium they are nearer the red. There is also some similarity in the distribution of the lines; this is particularly true of certain groups, e.g. the alkalis.

BALMER and also KAYSER and RUNGE have discovered numerical relations between the wave lengths of the lines of the same element. The first-named investigator found that the wave lengths of the hydrogen lines are expressed with striking accuracy by the formula

$$\lambda = A \frac{n^2}{n^2 - 4},$$

in which  $A$  is a constant (3647.20) and  $n$  stands for whole numbers from 3 to 15. This result naturally excited a desire to investigate the spectra of other elements, in which work the two last-named scientists have been especially prominent. It was found that the relation between the lines cannot be expressed in such a simple way as for those of hydrogen. In the first place it was necessary to employ a formula

$$\lambda^{-1} = A - Bm^{-2} - Cm^{-4},$$

which contains not merely one constant, as did that of BALMER, but three ( $A$ ,  $B$  and  $C$ ), and even then it does not represent the wave length with the same accuracy as does BALMER's formula for the hydrogen spectrum. Besides, it was impossible to represent the spectrum of a metal by one such formula, it being found necessary to divide the spectrum into *series*, for each of which the particular values of  $A$ ,  $B$  and  $C$  had to be calculated.\*

Finally, it was also found that for the elements of the first group of MENDELEEFF's system the different series (each element having several) consisted not of lines but of pairs (or triplets) of lines.

The impetus to all such investigations lies in the hope that a knowledge of the laws which govern the distribution of the spectrum lines of one and the same substance, on the one hand, and the variation in the distribution from substance to substance on the other hand, would throw some light on the nature and the kinetic condition of the atoms.

**266.** With the aid of spectroscopy it has been possible to determine what elements are present in the heavenly bodies. When light from the latter is passed through a prism, line spectra are obtained and these lines correspond in position to those of terrestrial elements. The composition of sunlight has been especially the object of a most extensive study. The spectrum of that body contains numerous black lines, known as FRAUNHOFER lines. Many of these correspond exactly to those of terrestrial substances. The fact that the lines in the solar spectrum are black is explained thus: The sun consists of a very hot central portion, which gives a continuous spectrum. This portion is surrounded by an atmosphere of incandescent vapors, whose temperature is below that of the interior. In this stratum are the elements whose lines are really bright, but appear dark in the solar spectrum. The light of the central portion is partially absorbed in this atmosphere, the absorbed lines being those of exactly the same wave length as the waves emitted by the atmosphere itself.

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\* According to Rydberg a more generally applicable formula is  $\lambda^{-1} = A - B(m + C)^{-2}$ .

On account of the greater intensity of the light from the interior the lines of the atmosphere ("reversing layer") appear dark on the light background. This phenomenon can be demonstrated in the following way: A little sodium chloride is introduced into a colorless gas-flame, making it yellow. In the spectroscope a bright yellow line is observed. If, however, a light with a higher temperature and a continuous spectrum (e.g. an electric arc) is placed behind the sodium flame and the latter is then observed through the spectroscope, a continuous spectrum of the electric light is seen and in the place of the sodium line there is a dark line. That portion of the light of the electric arc which has the wave length of the sodium line is completely absorbed by the sodium flame; the light intensity of the latter is, however, much lower, so that a dark line is formed on the bright background of the continuous spectrum.

By comparing the FRAUNHOFER lines with the spectra of terrestrial substances it has been found that the sun's atmosphere contains chiefly Fe, Na, Mg, Ca, Cr, Ni, Ba, Cu, Zn and H (the latter in enormous quantity). Moreover for 450 lines of the iron spectrum there are found to be corresponding dark lines in the sun's spectrum. On the other hand, the solar spectrum displays countless lines which are not known in terrestrial spectra.

267. We are led to presume that many of the elements to which these lines are due will also be revealed on the earth by more careful research, especially when we consider what a small part of the earth is known (see footnote, p. 8). This presumption has been strongly confirmed by the discovery of *helium* (p. 166). The principal line of the latter,  $D_3$ —so termed, because of its proximity to the double  $D$  line ( $D_1, D_2$ ) of sodium—was observed in the spectra of many fixed stars as well as in that of the sun before the element itself was identified on the earth. Helium was thus discovered in the stars before it was on the earth. It is a striking fact that it occurs in exceedingly large quantities in the fixed stars (according to spectrometric observations) while there is apparently only a very small amount of it on the earth.

### ZINC.

268. The most important zinc minerals are *calamine* ( $H_2Zn_2SiO_6$ ), *smithsonite* ( $ZnCO_3$ ), *sphalerite*, or *blende*, ( $ZnS$ ) and different oxides. The principal localities are Silesia, England, Belgium, Poland and, more recently, certain districts in the United States. To obtain the metal the ores are roasted—the gas ( $SO_2$ ) from the

sulphide ores is converted into sulphuric acid—yielding zinc oxide. This is mixed with coal and heated, forming carbon monoxide and zinc. The latter distills over and collects in the receiver together with a fine gray powder, *zinc dust*. This “dust” is a mixture of zinc oxide and zinc powder and is frequently used in the laboratory as a vigorous reducing agent.

The metal is bluish-white and has a specific gravity of 6.9–7.2. At ordinary temperatures it is brittle, but at 100–150° it becomes softer; it can then be beaten into plates. At the same time the specific gravity rises to 7.2 and the metal becomes firmer. At 200° it again becomes brittle and can be easily pulverized. It melts at 433° and boils at 920°. The metallic vapor has a specific gravity of 33.8 ( $H = 1$ ); hence its molecular weight is 67.6. Since the atomic weight, as deduced from DULONG and PETIT’S law, is 65.4, the molecule in the vaporous state can contain only one atom. The same is true of the related metals cadmium and mercury. Zinc is permanent in the air, since it becomes firmly coated with a protective layer of oxide. Zinc dust decomposes water. When heated to boiling in the air the metal burns to zinc oxide, producing an intensely bright light. It is dissolved very easily by hydrochloric or sulphuric acid with the evolution of hydrogen; it is an interesting fact, however, that when a piece of absolutely pure zinc is placed in either of these acids no hydrogen is generated. If this piece of zinc is brought in contact with a platinum wire, effervescence begins at once, not from the surface of the zinc, however, but from that of the wire, and zinc goes into solution. Written in ions the process is



and its explanation is just the same as that given in § 203, for the formation of a “lead tree.” In this case also the zinc drives cations into the solution with great force, itself thus assuming a negative charge, with which hydrogen ions can be discharged. The only difference seems to be that these hydrogen ions discharge themselves at the platinum instead of at the zinc. However, this difference is not real since in the case of the lead tree the fresh portions of lead are deposited on the outermost parts of it. The perfect analogy is made still clearer by a somewhat modified form of the experiment.

When, on the one hand, a plate of amalgamated zinc and one of platinum are connected by a metallic wire and dipped in dilute sulphuric acid (Fig. 74) hydrogen is evolved from the platinum plate and when, on the other hand, a plate of amalgamated zinc and one of lead are similarly connected and dipped in a dilute solution of lead nitrate (Fig. 75) lead crystals are deposited not on the

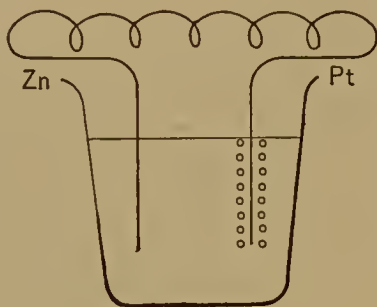


FIG. 74.

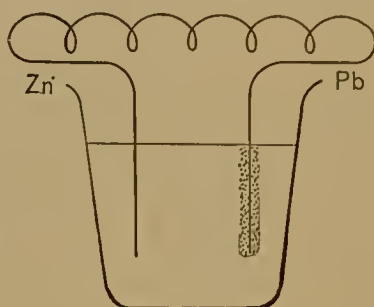


FIG. 75.

zinc but on the lead. In both cases the negative charge of the zinc goes through the wire to the other plate, on which the ions of hydrogen, or lead, as the case may be, can discharge themselves.

Metallic zinc—often called *spelter* in commerce—has numerous uses. For instance, zinc plates are very extensively used for roofing. Iron is frequently coated with zinc to prevent rusting; it is then known as *galvanized iron*. Further, zinc is a constituent of many alloys, e.g. brass (§ 242).

**269. Zinc oxide,  $ZnO$ ,** is usually prepared by igniting the basic carbonate. On being heated it turns yellow; on cooling, the original white color returns. It is employed as a pigment under the name *zinc white*, or *Chinese white*.

**Zinc hydroxide,  $Zn(OH)_2$**  is precipitated by alkalis from the solution of a zinc salt as a white gelatinous mass, soluble in the alkalis as well as ammonia; however the reason is different in the two cases. In the presence of alkalis zinc hydroxide behaves as a weak acid; it forms  $ZnO_2^{--}$  anions and the cations  $2H^+$ , which yield a salt  $Zn(OK)_2$  with the alkali in the ordinary way (§ 66). When treated with ammonia, however, a complex zinc-ammonia ion is formed, which is soluble.

**Zinc chloride,  $ZnCl_2$ ,** can be obtained by heating zinc in a current of chlorine or by dissolving zinc in hydrochloric acid and evaporating the solution. In the latter case some oxychloride is

formed, however. Zinc chloride melts on heating and distills at  $680^{\circ}$ . It is very hygroscopic and is often used for splitting off water from organic compounds. On adding zinc oxide to a concentrated zinc chloride solution a soft mass is obtained, which soon becomes hard because of the formation of the basic chloride  $\text{Zn} < \frac{\text{OH}}{\text{Cl}}$ . Ammonia unites with zinc chloride to form various compounds.

**Zinc sulphate**,  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ , crystallizes in well-developed crystals, which are isomorphous with the analogous compounds  $\text{MgSO}_4 \cdot 7 \text{ aq}$ ,  $\text{FeSO}_4 \cdot 7 \text{ aq}$ , etc. It is prepared commercially by carefully roasting zinc blende.

**Zinc sulphide**,  $\text{ZnS}$ , is completely precipitated by hydrogen sulphide from solutions of its salts to which sodium acetate has been added to neutralize the acid set free from the zinc salt. In the absence of sodium acetate it is still partially precipitated, even from solutions of the neutral salts of strong acids.

This is not the case with the salts of the other metals belonging to the same analytical group as zinc, e.g. with the ferrous and manganese salts. The difference is due to the greater insolubility of zinc sulphide. When hydrogen sulphide is passed into a zinc solution, which contains of course Zn-ions and acid anions,  $\text{H}_2\text{S}$ -molecules and H- and S-ions are introduced into the liquid so that we have side by side the ions :



Especially if the zinc solution is concentrated, the solubility product of the Zn- and S-ions is soon reached so that  $\text{ZnS}$  must be deposited. This action however will soon reach a limit, on account of the H-ions which stay in the solution and almost completely suppress the ionization of the hydrogen sulphide molecules still present. By the addition of an excess of sodium acetate, however, these free H-ions find occasion to combine with the acetic anions, and this combination will be almost complete when an excess of the latter ions is present. The concentration of the H-ions thus becomes so slight that the zinc-sulphide must all be deposited. If, however, the solubility product of the sulphide is not so small, as in the case of ferrous and manganese sulphides, the slight ionization of the  $\text{H}_2\text{S}$  renders it impossible for the solubility product to be reached, or, in other words, the sulphides will not be precipitated. Zinc, by reason of the solubility of its sulphide thus assumes an intermediate position between the metals that are not precipitated by hydrogen sulphide and those that are. The solubility of the sulphides must decrease in the series  $\text{FeS} \dots \text{ZnS} \dots$

CuS ; the difference between these two analytical groups is thus not sudden or sharp but gradual.

### CADMIUM.

**270.** Cadmium is very frequently found in zinc ores. Being more volatile than zinc it distills over first in the extraction of such ores. It is obtained pure by repeated distillation or by conversion into the sulphide, which is insoluble in dilute acids and can therefore be separated by the latter from zinc sulphide.

Cadmium is a white, rather soft metal; sp. g., 8.6; m.-pt.,  $315^{\circ}$ ; b.-pt.,  $778^{\circ}$ . It is unaffected by the air but burns on heating, forming a brown cloud of oxide. It is difficultly soluble in dilute hydrochloric and sulphuric acids, but readily soluble in dilute nitric acid. The cadmium molecule in the gaseous state contains only one atom.

Cadmium oxide, CdO, is obtained as stated above and also by heating the carbonate or hydroxide. It is an amorphous brown powder. Cadmium hydroxide,  $\text{Cd}(\text{OH})_2$ , is insoluble in caustic potash or caustic soda but soluble in ammonia, on account of the formation of a complex ion. Cadmium chloride,  $\text{CdCl}_2$ , crystallizes with two molecules of water and can (unlike zinc chloride) be dried without decomposition. Cadmium sulphide, CdS, is characterized by a bright yellow color (it is used as a pigment). It is insoluble in acids. The sulphate,  $\text{CdSO}_4$ , usually crystallizes out of its aqueous solution as  $3\text{CdSO}_4 + 8\text{H}_2\text{O}$ . There is also a salt  $\text{CdSO}_4 + 7\text{H}_2\text{O}$ , which is analogous in composition to the sulphates of magnesium, zinc, iron, etc.

### MERCURY (Quicksilver).

**271.** Mercury is the only metal that is liquid under ordinary conditions. It occurs in nature in *cinnabar*, HgS, and also *native*. The chief localities are Almaden in Spain, Idria in Illyria, Mexico, Peru, California, China and Japan. To obtain mercury from cinnabar the latter is roasted in furnaces, sulphur dioxide and mercury being formed. The mercury vapor is condensed either in large chambers or in peculiarly shaped earthen retorts, or pipes, called *aludels*. It is brought on the market in iron flasks.

The commercial product is not pure, containing more or less of other metals in solution (e.g. lead, copper, etc.). Such impurities can be readily



detected by the fact that they make the mercury adhere to a glass vessel. A suitable process of purification consists in letting it fall in fine drops through a long column of nitric acid (sp. g., 1.1) as in Fig. 76. The foreign metals are thus completely dissolved, while almost no mercury is lost by solution, because these foreign metals precipitate mercury from its salt solutions. After being washed with water the metal is dried and, if absolute purity is desired, it is then distilled *in vacuo*. But a vacuum distillation by itself is insufficient, for some lead goes over with it.

*Physical Properties.*—Mercury solidifies at  $-39.4^{\circ}$  and boils at  $360^{\circ}$ . Even at ordinary temperatures it is somewhat volatile, especially under reduced pressure; when gold-leaf is suspended in a bottle over mercury, for instance, it becomes white in time. The metal has a specific gravity of 13.595 at  $0^{\circ}$ . The vapor density is 99.36 for  $H = 1$ ; hence the molecule weighs 198.72. This number also represents the atomic weight, as has been found from molecular weight determinations of many volatile mercury compounds.

*Amalgams.*—Many metals have the property of dissolving in mercury or forming compounds with it. These metal solutions or compounds are called amalgams. Besides by the direct contact of the two metals they can sometimes also be obtained by allowing mercury to act on the solutions of metal salts, e.g. silver amalgam can thus be prepared. Some metals, such as tin, dissolve in mercury with heat absorption; others like potassium and sodium with great heat evolution and vigorous action. If a great excess of mercury is used, the amalgams are liquid, otherwise solid. Sodium amalgam is exceedingly firm when it contains more than 3% Na.

*Chemical Properties.*—At ordinary temperatures the metal is

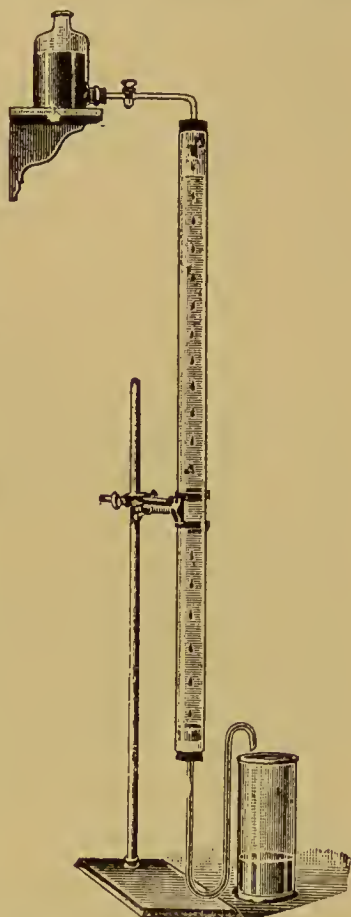


FIG. 76.—PURIFICATION OF MERCURY.

not affected by the air; at higher temperatures it takes up oxygen to form the oxide  $\text{HgO}$ , which, however, splits up again into its elements on farther heating. Dilute hydrochloric and sulphuric acids do not attack it at ordinary temperatures and dilute nitric acid acts only in the presence of nitrogen dioxide (see § 127). Mercury unites instantaneously with the halogens and sulphur.

Mercury forms two sets of salts, *ous* and *ic*, the former being derived from *mercurous oxide*,  $\text{Hg}_2\text{O}$ , and the latter from *mercuric oxide*,  $\text{HgO}$ .

### Mercurous Compounds.

**272. Mercurous oxide**,  $\text{Hg}_2\text{O}$ , is dark brown. It is precipitated from the solution of a mercurous salt by caustic soda. It decomposes at as low a temperature as  $100^\circ$  or in the light, yielding  $\text{HgO}$  and  $\text{Hg}$ .

**Mercurous chloride**,  $\text{Hg}_2\text{Cl}_2$ , *calomel*, can be prepared in the wet way by precipitating a dissolved mercurous compound with a chloride, or in the dry way by subliming a mixture of mercuric chloride and mercury. It is a white powder, insoluble in water, but turns dark in the light on account of the separation of metallic mercury. Ammonia blackens it by forming a mixture of mercuric ammonium chloride,  $\text{NH}_2\text{HgCl}$ , and finely divided mercury:



Calomel is frequently used as a medicament.

The vapor density of calomel has been found to be 117.6 ( $\text{H} = 1$ ), which corresponds to the molecular formula  $\text{HgCl}$ . When calomel evaporates, however, a dissociation into  $\text{HgCl}_2$  and  $\text{Hg}$  occurs; these products unite again on cooling but they can be previously separated by diffusion. It is for the above reason that the vapor density was found to be half the amount calculated for  $\text{Hg}_2\text{Cl}_2$ ; hence the correct formula of calomel is  $\text{Hg}_2\text{Cl}_2$ .

**Mercurous bromide and iodide** are even less soluble than the chloride. The solubility decreases, as in the case of silver, with an increase in the atomic weight of the halogen.

**Mercurous nitrate**,  $\text{HgNO}_3$ , is formed when cold dilute nitric acid acts on an excess of mercury. It is hydrolytically dissociated

by water, a yellow basic salt  $\text{Hg}_2 < \begin{matrix} \text{OH} \\ \text{NO}_3 \end{matrix}$  being deposited. It therefore dissolves without decomposition only in dilute nitric acid. The mercurous ion is evidently only very feebly basic. A solution of mercurous nitrate is slowly oxidized by the oxygen of the air to the mercuric salt, but the addition of a little mercury reconverts it into the lower form.

### Mercuric Compounds.

**273. Mercuric oxide,  $\text{HgO}$ ,** is red and crystallized when prepared by heating mercury or mercury nitrate, but yellow and amorphous when precipitated from solutions by a hydroxide of potassium or sodium. The difference between these forms seems to be due only to a difference in the coarseness of their grains. Mercuric oxide turns black on heating and red on cooling.

**Mercuric chloride,  $\text{HgCl}_2$ ,** corrosive sublimate, is manufactured on a large scale by heating a mixture of common salt and mercuric sulphate; it sublimes over, whence its name. At room temperature 1 part  $\text{HgCl}_2$  dissolves in 15 parts  $\text{H}_2\text{O}$ . It is more soluble in alcohol. The acid reaction of its aqueous solution indicates hydrolytic dissociation; if sodium chloride or potassium chloride is added to the liquid, the reaction becomes neutral because of the formation of a double salt  $\text{HgCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O}$ . This is more soluble in water than sublimate itself.

**Mercuric iodide,  $\text{HgI}_2$ ,** is yellow when it is first precipitated from the solution of a mercury salt by potassium iodide, but it soon becomes red. If this modification is heated, it passes over into a yellow form at  $150^\circ$ , the original red color returning on cooling, however. There is evidently a transition-point here.

A similar transition-point is shown by the double salt  $\text{Cu}_2\text{I}_2 \cdot 2\text{HgI}_2$  which changes its color from red to brown at a temperature below  $100^\circ$ ; it also displays the peculiarity that the transition proceeds very fast in both directions, whereas most such processes are very slow. For this reason it has been suggested that the ends of the axles of railway carriages be coated with this substance so as to show when they become overheated.

Mercuric iodide dissolves readily in potassium iodide solution. **N E S S L E R'S s o l u t i o n,** a very valuable reagent in testing for ammonia, is made by mixing the above mercuric iodide solution with caustic potash. It should be noted, however, that many

organic nitrogen compounds give much the same coloration as ammonia with NESSLER'S solution.

**Mercuric cyanide**,  $\text{HgCy}_2$ , is obtained by boiling Prussian blue with mercuric oxide. It crystallizes in fine large colorless crystals.

274. The mercuric halides, in contrast to the other salts of the mercuric ion, are only slightly ionized in aqueous solution. For this reason they exhibit some peculiar reactions. On mixing a mercuric solution with one of a chloride, for instance, considerable heat is given off because undissociated  $\text{HgCl}_2$  molecules are formed, while the mixture of solutions ordinarily obeys the law of thermoneutrality (§ 238, 2).—Again, if mercuric oxide is shaken with a solution of chloride, bromide or iodide of potassium, the liquid becomes strongly alkaline because of the liberation of potassium hydroxide. This is due partly to the slight ionization of the mercury halides and partly to the combination of the latter with the excess of alkali halide to form very stable alkali mercuric halides. The stability of these complex compounds increases with rising atomic weight of the halogen.—The same cause explains the reverse fact, viz., that the halogen compounds of mercury are only with difficulty decomposed by alkalis. In order to precipitate all the mercury from mercuric chloride a large excess of potassium hydroxide must be employed; mercuric iodide and mercuric cyanide cannot be decomposed by potassium hydroxide alone. Mercuric cyanide is so little ionized that its conductivity can hardly be measured; hence it does not give any of the ordinary mercury reactions, except the formation of the sulphide (since the latter is so very insoluble). This cyanide can be regarded as a type of compounds rendered inactive because of non-ionization.

The mercuric halides (especially corrosive sublimate) are very strong antiseptics. It is an interesting fact that in this respect also, they become more effective as their ionization increases. The chloride is a more powerful antiseptic than the cyanide. The addition of metal chlorides diminishes the ionization of sublimate and at the same time reduces its disinfecting ability.

The reason why the mercuric chloride for use in sublimate tablets is nevertheless mixed with an excess of common salt is partly that the sublimate may be dissolved more rapidly and also because such solutions keep longer than those of the pure sublimate, especially when prepared with well-water.

**Mercuric nitrate**,  $\text{Hg}(\text{NO}_3)_2$ , forms basic salts very readily: on diluting its solution in nitric acid with water there is deposited a compound  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgO} \cdot \text{H}_2\text{O}$ , which is converted into pure mercuric oxide by boiling with water. This shows that the bivalent mercuric ion also is very feebly basic.

**Mercuric sulphate** is not soluble in water but is converted by the latter into a basic salt. In the presence of much water the yellow  $\text{HgSO}_4 \cdot 2\text{HgO}$  is formed. With the sulphates of the alkalies it forms double salts, e.g.  $\text{HgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , which are isomorphous with the corresponding double salts of magnesium (§ 255), iron, etc.

**Mercuric sulphide**,  $\text{HgS}$ , is black when precipitated from solution; on being heated in the absence of air it sublimes in dark-red crystals, which are similar to natural cinnabar and are used as a pigment (*vermilion*).

### Summary of the Group.

275. Here again a gradual change in the physical properties is to be seen as the atomic weight rises. The following small table sets it forth:

	Be	Mg	Zn	Cd	Hg
Atomic weight.....	9.1	24.36	65.4	112.4	200.3
Specific gravity.....	1.64	1.75	6.9	8.6	13.6
Melting-point.....	> 900°	> 700°	412°	320°	- 39.4°
Boiling-point.....	.....	> Zn	920°	778°	360°
Atoms in molecule.....	.....	.....	1	1	1

In respect to the chemical properties it should be noted that all of these elements are bivalent. Mercury, however, can be considered as univalent in its ous-compounds. Their sulphates unite with those of the alkalies to form double salts of the same type,  $\text{RSO}_4 \cdot \text{R}'_2\text{SO}_4 \cdot 6 \text{ aq}$  ( $\text{R}' = \text{K}, \text{Na}, \text{NH}_4$ ); the beryllium double salt alone crystallizes with 3 aq. The hydroxides of this group are soluble in ammonia with the formation of complex ions, or they yield insoluble metal-ammonia compounds (Hg).

The neutral salts have a tendency to go over into basic salts. This is especially marked in mercury; in the case of cadmium it is, strange to say, very weak.

With the halogen compounds of the three related metals Zn, Cd and Hg the electrolytic dissociation is small; it decreases as the atomic weight of the metal rises and is very slight in the case of mercury.

## ELECTROCHEMISTRY.

276. As early as the beginning of the nineteenth century, when DAVY isolated the alkali metals by means of the electric current (§§ 223 and 227), it was known that there is an intimate relation between electrical and chemical phenomena. BERZELIUS even went so far as to suppose that affinity could be perfectly explained by assuming that the atoms are electrically charged and that this is why they attract or repel each other. For a long time the galvanic element has been known as a means of converting chemical energy into electrical. It was not until 1889, however, that a theoretical explanation of the connection between chemical and electrical phenomena was offered; this explanation by NERNST is not only a very satisfactory one but it also affords an insight into numerous chemical phenomena.

When a metal comes in contact with the aqueous solution of one of its salts a difference in potential develops between the two. For this phenomenon NERNST presents the following explanation, which is of fundamental importance to electrochemistry. Just as a liquid continues to evaporate at its surface until the pressure of the vapor becomes equal to the vapor-tension of the liquid, so a salt must continue to dissolve in water (evaporation and solution being analogous processes) until the osmotic pressure of its solution balances the solution tension of the salt. Now, according to NERNST, every metal also has a certain tendency, dependent only on its chemical character, to force its atoms into solution as ions. This force, called the *solution tension*, comes into action when the metal is immersed in an electrolyte and its strength is the less, the more cations of the metal are already in the solution. If  $P$  represents the solution tension of a metal and  $p$  the osmotic pressure of the cations in the solution, there are three possibilities to be distinguished:

(1)  $P > p$ . The metal then behaves like a salt in contact with its own unsaturated solution. It forces cations into the solution of the electrolyte, so that the solution becomes positively charged and the metal has to take on a negative charge. No matter how much the value of  $P$  may exceed that of  $p$ , the number of cations which the metal forces into solution is necessarily small, for an equilibrium must soon be established inasmuch as the negatively

charged metal exerts an attraction on its positively charged ions and just as many metal ions will soon be redeposited on the metal as are driven into the solution. However, if the free positive and negative electricities acquired by the electrolyte and the metal are conducted away by a connecting wire the metal will again send cations into the solution, and this action will continue till  $p$  reaches the value of  $P$ .

(2)  $P = p$ . There can be no potential difference.

(3)  $P < p$ . In this case the metal corresponds to a salt introduced into its supersaturated solution. Cations are now deposited on the metal and charge it positively, the electrolyte becoming negative. Here also a state of equilibrium must soon arise since the negatively charged electrolyte tends in turn to drive the positive metal ions back into solution.

The relation between the potential difference  $E$  and the magnitudes  $P$  and  $p$ , NERNST expresses by the equation:

$$E = \frac{RT}{n} l \frac{P}{p}, \quad . . . . . (1)$$

in which  $R$  is the gas constant,  $T$  the absolute temperature,  $n$  the valence of the metal ions and  $l$  the natural logarithm.

From this equation it follows, among other things, that  $E$  increases in arithmetical progression as  $p$  decreases in geometrical progression. If  $E$  is expressed in volts,  $R = 0.860 \times 10^{-4}$ . If we make  $T = 291$ , i.e.  $273 + 18$  ( $18^\circ$  taken as the room temperature), and introduce BRIGGS logarithms, we have:

$$E = \frac{0.0576}{n} \log \frac{P}{p}.$$

If, for example, the ionic concentration grows ten times smaller,  $E$  increases by only  $\frac{0.0576}{n}$  volts; it is thus seen that the potential difference is not much affected by changes in the concentration of the electrolyte, even though they be quite large.

On bringing together two different metals and their salt solutions an element, or cell, of the DANIELL type is obtained (copper in copper sulphate and zinc in zinc sulphate, the two pairs separated by a porous partition). The electromotive force of such a cell is found from the difference of the two values of  $E$ , i.e.

$$E = \frac{RT}{n} \left( l \frac{P_1}{p_1} - l \frac{P_2}{p_2} \right), \quad . . . . . (2)$$

when both metals have the valence  $n$ .

In such a cell with closed circuit there are differences of potential not only between metal and solution but also between the two liquids and between the two metals. Experience has shown both of the latter to be very small in comparison to the former, however, so that they may be disregarded.

Leaving the solution tensions  $P_1$  and  $P_2$  out of consideration,  $E$  therefore depends on the values of the osmotic pressure  $p_1$  and  $p_2$  of the metal-ions. If  $p_2$  can be made extremely small, so that  $l \frac{P_1}{p_1} < l \frac{P_2}{p_2}$ ,  $E$  becomes negative, i.e. the current must alter its direction. This can be demonstrated as follows:

In a DANIELL cell, in which the osmotic pressure of the zinc ions ( $p_1$ ) is seldom very different from that of the copper ions ( $p_2$ ), the current goes from the copper through the connecting wire to the zinc, for the solution tension ( $P_1$ ) of the zinc is much larger than that ( $P_2$ ) of the copper (see below). Now the concentration of the copper ions can be made several powers of ten smaller by adding potassium cyanide to the copper sulphate solution, for by this means the very slightly ionized complex  $(\text{Cu}_2\text{Cy}_4)''$  is formed (§ 243). This addition actually reverses the direction of the current. Neither the precipitation of the copper by potassium hydroxide nor the precipitation by ammonium sulphide reduces the concentration of the copper ions enough to produce this effect.

Since equation 2 can also be written

$$E = \frac{RT}{n} \left( l \frac{P_1}{P_2} - l \frac{p_1}{p_2} \right),$$

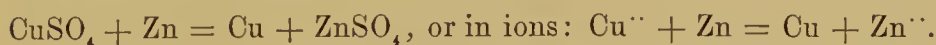
and, when  $p_2 = p_1$ , the last expression becomes zero, it is apparent that the electromotive force of a DANIELL cell is mainly determined by the ratio of the solution tensions of the metals. *A galvanic cell can be regarded as a machine driven by the electrolytic solution tensions of the metals.*

The introduction of this conception of solution tension and the ideas connected with it has led to an altogether clearer understand-



ing of the chemical processes of galvanic cells, as well as of the way in which the current is formed in them.

Galvanic cells may be divided into two classes, *reversible* and *non-reversible*. The DANIELL belongs to the first class. It produces a current because the solution tension of the zinc exceeds that of the copper. The zinc sends its positively charged ions into the sulphate solution and itself becomes negative. On the other hand, the copper ions, on passing over into atoms and precipitating themselves on the copper plate, transfer their positive charges to the latter, which thus becomes the positive pole. Chemically the process amounts to the simultaneous solution of zinc and precipitation of copper:



If a current is sent through the DANIELL cell in the opposite direction, ions will enter into solution at the copper plate because the latter acquires a positive charge, and the zinc ions will be forced to deposit themselves on the zinc, for the reverse current charges the zinc negatively so that it attracts the zinc ions. It is therefore possible by passing a reverse current through the cell to restore it to its original condition,—hence the term reversible.

One of the most important styles of reversible batteries is the **accumulator**, or storage-battery (Fig. 77). This consists of a glass jar in which lead plates are suspended so that they dip into dilute sulphuric acid. These plates are coated alternately with lead peroxide (positive) and lead sulphate (negative). The positive plates are all connected with each other, as are also the negative ones. (From a large number of such cells a battery is constructed by connecting the positive pole of each cell with the negative pole of the adjoining one.) If a current is passed through the system so that it enters at the lead peroxide plate and goes through the sulphuric acid to the other plate, lead peroxide collects on the positive plate while on the other, the cathode plate, the lead sulphate is converted into spongy lead. By this process the accumulator is charged. There



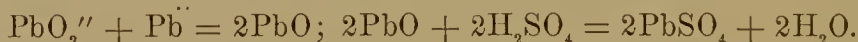
FIG. 77.—ACCUMULATOR.

upon, if the poles are connected (by a wire), the opposite process goes on; the lead peroxide is reduced at the one plate and the spongy lead is converted into lead sulphate at the other. During the discharge the peroxide plate is again positive, the lead plate negative.

The chemical process in the accumulator cell is therefore expressed by:



The generation of the current has been explained in various ways; one is as follows: The lead peroxide on the anode plate has a certain solution tension, and hence goes into solution as negatively charged  $\text{PbO}_2''$  ions. Thereby it of course imparts to the plate itself a numerically equivalent positive charge. These bivalent  $\text{PbO}_2''$  ions encounter positively charged  $\text{Pb}''$  ions at the cathode plate, which are being sent by it into the solution; the cathode plate charges itself negatively at the same time. The two sorts of ions now combine to form electrically neutral  $\text{PbO}$  molecules, which yield lead sulphate with the sulphuric acid present:

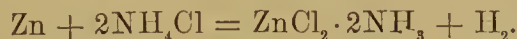


Among the non-reversible cells are the BUNSEN and the LECLANCHÉ. A reverse current does not restore these to their original condition and their electromotive force  $E$  cannot be calculated by the above formula; nevertheless the general principles of the pressure theory can be applied to explain the production of the galvanic current by these cells.

The arrangement of the BUNSEN cell—an amalgamated zinc plate dipped in sulphuric acid and a carbon cylinder in nitric or chromic acid—is well known. From an electrochemical standpoint the generation of hydrogen from zinc and sulphuric acid amounts to a transfer of the charges of the hydrogen ions of the dilute acid to the zinc atoms and an escape of hydrogen in the form of discharged molecules. In the BUNSEN cell, however, most of the hydrogen ions find an opportunity to give up their positive charges to the carbon cylinder and exercise a reducing action on the nitric or chromic acid. On the other hand the zinc plate sends positively charged zinc ions into the solution to the

same extent as hydrogen ions disappear, the zinc plate itself acquiring a negative charge.

The LECLANCHÉ cell consists of a zinc bar in concentrated ammonium chloride solution and a porous earthenware cylinder immersed in the same solution and containing some manganese peroxide and a stick of carbon for conducting off the current. Here again the zinc goes into solution:



The hydrogen ions discharge themselves at the carbon and reduce the peroxide. In this case also the carbon is the positive, the zinc the negative, pole.

277. Just as in galvanic cells chemical energy is transformed into electrical energy, so there is reason to suppose that reactions between ions in general are capable of producing an electric current if the conditions are suitable. A few examples of this may be cited.

For these experiments a cell devised by LÜPKE is very satisfactory (Fig. 78). It consists of two glass vessels  $Z_1$  and  $Z_2$ , to the bottoms of which the platinum electrodes  $k_1$  and  $k_2$  are attached. The vessels are connected by means of the wide siphon  $H$ . The wires  $A$  and  $K$  lead to a galvanoscope. To show that electrical energy can be obtained by the oxidation of the stannous to the stannic chloride an acidulated stannous chloride solution (11.2 : 100) is introduced into  $Z_1$  and an acidulated normal sodium chloride solution into  $Z_2$ ; the siphon also is filled with the latter solution. As soon as a few drops of chlorine water or a solution of auric or mercuric chloride are allowed to fall from a pipette upon the electrode ( $k_2$ ) in the salt solution, the galvanoscope indicates a current in the wire circuit from  $K$  to  $A$ . Now, in order that the bivalent ion  $\text{Sn}^{++}$  may become quadrivalent ( $\text{Sn}^{++++}$ ) it must acquire two more positive charges and

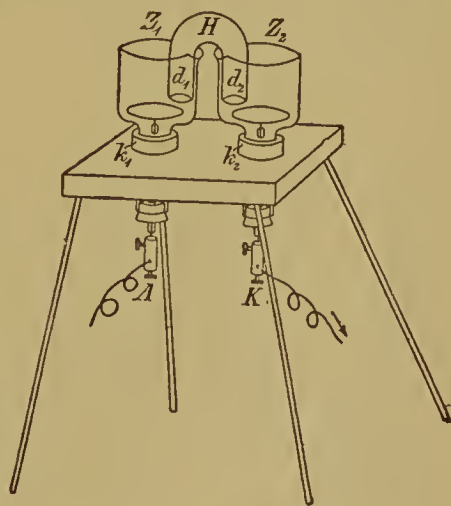


FIG. 78.—LÜPKE CELL.

this requires the addition of two chlorine ions. These are at once supplied by the mercuric or auric chloride. The metallic ions (Hg or Au) deposit themselves on  $k_2$  and impart to the latter a positive charge, which, if conducted by means of the wire circuit  $k_1$ , is at the disposal of the  $\text{Sn}^{++}$  ions. If free chlorine is added, it splits up into ions, as a result of which positive electricity is imparted to  $k_2$  and this flows through the wire circuit back to  $k_1$  and raises the potential of the  $\text{Sn}^{++}$  ions.

The precipitation of silver chloride according to the equation:



can be made to produce an electromotive effect by laying a polished piece of sheet silver on each platinum electrode of the above apparatus and filling  $Z_1$  with sodium chloride solution and  $Z_2$ , as well as the siphon, with an equimolecular sodium nitrate solution. As soon as a crystal of silver nitrate is placed on the electrode  $k_2$  (in the nitrate solution) a current is detected. Previous to the introduction of the silver nitrate crystal both pieces of silver because of their solution tensions drive equal amounts of silver ions into solution, but equilibrium is very soon reached (§ 276). The crystal, however, has caused the formation, around the electrode  $k_2$ , of a concentrated silver solution, whose osmotic pressure far exceeds the solution tension of the metal. As a result silver ions are thereupon deposited on  $k_2$  and this electrode becomes positively charged; this charge passes through the wire circuit to  $k_1$ . The result of this is the sending of more silver ions into the salt solution around  $k_1$ , but their concentration very soon becomes so great that the solubility product of silver chloride is exceeded and the latter is precipitated on the silver plate in  $Z_1$ .

The fact that electrical energy can be obtained by the neutralization of sulphuric acid is capable of demonstration with the aid of the same apparatus. To this end a  $\frac{1}{2}$ -normal sulphuric acid is introduced into  $Z_2$  and a  $\frac{1}{2}$ -normal potassium sulphate solution into  $Z_1$  and the siphon. If a large piece of palladium foil (about 4 cm<sup>2</sup>) that has been saturated electrolytically with hydrogen is placed on the platinum disk of the electrode  $k_2$  and touched for a few moments with a stick of caustic potash, bubbles of hydrogen will rise from the platinum plate of the other electrode ( $k_1$ ) and

the needle of the galvanoscope will indicate the passage of a powerful current outward from  $k_1$ . The hydrogen of the palladium foil sends positive ions into the solution, which, however, forthwith unite with the OH-ions of the potassium hydrate to form neutral water. By the emission of these positive ions  $k_1$  acquires a negative potential, which flows out through the external circuit to  $k_2$ . The hydrogen ions of the sulphuric acid surrounding this electrode are thus afforded an opportunity of discharging themselves against this negative charge so that hydrogen is given off in the free state.

In the combination of chlorine (or oxygen) and hydrogen chemical energy can also be transformed into electricity. To accomplish this, two tubes sealed at the top and fitted there with platinum electrodes, reaching almost to the open end of the tubes, are filled, one with hydrogen and the other with chlorine (oxygen) and inverted in dilute sulphuric acid. On connecting the electrodes by a wire a strong current traverses the circuit. The gases absorbed in the platinum electrodes drive their ions into the surrounding liquid, making the H-electrode negative and the Cl(O)-electrode positive. The ions of hydrogen and chlorine dissolve in the dilute sulphuric acid, however. This apparatus is called GROVE'S gas battery and was known long before a satisfactory explanation of it could be given.

In conclusion we may cite a case where a current is obtained by the partial discharge of ions. If a piece of sheet iron is introduced into a sodium chloride solution from above and a similar piece of platinum is laid on the bottom, a galvanoscope inserted in the circuit between the metals shows no current; but if the platinum at the bottom is surrounded by ferric ions by dropping in a little solid ferric chloride, a current is immediately formed. The ferric ions send through the wire one-third of their (positive) charge to the iron plate and this enables the iron to keep on sending ferrous ions into the liquid until all the ferric chloride added has been converted into ferrous chloride.

It is characteristic of all these various cells that *the reacting substances are separate from each other*. In the oxidation of stannous chloride by mercuric chloride the latter was not put in the vessel with the stannous chloride but in the other; in the precipitation of silver chloride the silver nitrate was not put with the

sodium chloride solution but with the sodium nitrate solution, and so on. The reaction took place only because one sort of ions transferred their electrification wholly or in part through the wire circuit to the other electrode, where it either converted atoms into ions or raised existing ions to a higher potential or, possibly, changed ions of opposite potential sign to neutral atoms.

Since we know that chemical reactions can under suitable conditions produce an electric current, we can, conversely, regard the existence of such a current as an indication of the occurrence of a chemical reaction. COHEN has made use of this fact in determining electrically the transition-points of hydrous salts and other systems. Let us take, for example, a salt which loses its water of crystallization at a definite temperature, e.g. Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10 \text{ aq}$ ; this has a transition-point at about  $33^\circ$ , where the anhydrous salt becomes capable of permanent existence. Now it is possible for the anhydrous salt to remain in contact with its saturated solution in an unstable condition after the system has been cooled a few degrees below  $33^\circ$ ; the reverse is also true of the hydrous salt. Since these solutions are in contact with different solid phases (one with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and the other with  $\text{Na}_2\text{SO}_4$ ) they do not have the same concentration; at the transition-point, however, these concentrations become equal, for, since both solid phases are in contact with the solution in each case, the solubility has become the same. In his electrical method COHEN uses the difference in concentration of the solutions which are saturated in respect to the two solid phases to form a galvanic cell. This can be done as follows: In the bottom of each of the cylinders *A* and *B* (Fig. 79) there is a little mercury. A platinum wire is fused into each cylinder and the two are connected by means of a metallic wire. On top of the mercury is some insoluble mercurous sulphate; above this in *A* is a paste of  $\text{Na}_2\text{SO}_4 \cdot 10 \text{ aq}$  and water, in *B* is a similar mixture of water and  $\text{Na}_2\text{SO}_4$ . Below the transition-point the solution in *B* is in the unstable condition and more concentrated than that in *A*, which is stable. The result is that sodium ions diffuse through the siphon from the concentrated to the dilute solution, while at the same time an equivalent amount of  $\text{SO}_4$ -ions in *B* combines with part of the mercury to form mercurous sulphate, the negative charge of the sulphate ions being transferred to the mercury remaining. Thus an electric current is produced, which

passes through the wire circuit from the dilute to the concentrated solution. Its direction and intensity can be determined by inserting a galvanometer in the circuit.

Now, suppose that the whole apparatus is gradually warmed; the concentrations in *A* and *B* will approach each other as the temperature nears the transition-point and at this point they

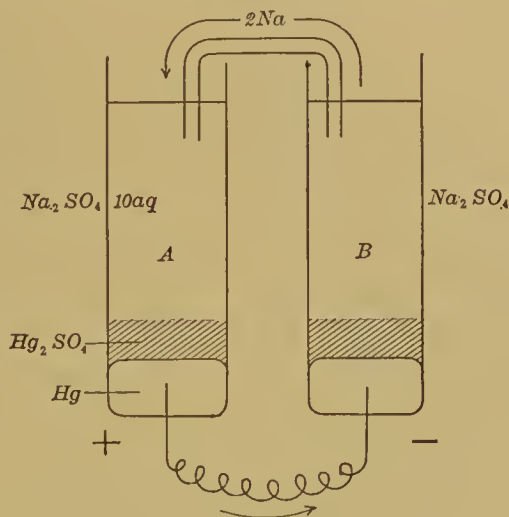


FIG. 79.

become equal. The intensity of the current will therefore decrease steadily till the transition-point is reached, when it is zero. If the temperature is raised still higher the solution in *A* will become unstable and more concentrated than that in *B*, which latter will then be the stable solution; as a result the direction of the current will be reversed. In this way it is possible to determine the transition-point very accurately.

278. As was remarked in § 276, the electromotive force which can be obtained from chemical reactions depends in large measure on the solution tensions of the metals. A knowledge of the latter is therefore of very great importance. It can be acquired with the aid of the equation previously given:

$$E = \frac{RT}{n} \ln \frac{P}{p};$$

*E*, the difference of potential between a metal and the aqueous solution of one of its salts can be measured. All the other quantities of this equation are known with the exception of *P*, which

can therefore be calculated. The following brief table indicates some of the results for different metals:

Metal.	Valence.	Solution-tension $P$ in Atmospheres.	Quantity (in grams) of the Metal in 1 Liter Sulphate Solution necessary to compensate $P$ .
Mg	2	$0.115 \times 10^{14}$	$1.238 \times 10^{13}$
Zn	2	$1.786 \times 10^{19}$	$0.520 \times 10^{20}$
Cd	2	$0.599 \times 10^7$	$3.166 \times 10^7$
Fe	2	$1.068 \times 10^4$	$2.676 \times 10^4$
Pb	2	$1.950 \times 10^{-2}$	$1.805 \times 10^{-1}$
Cu	2	$2.228 \times 10^{-19}$	$0.313 \times 10^{-20}$
Hg	1	$2.178 \times 10^{-16}$	$0.390 \times 10^{-16}$
Ag	1	$0.567 \times 10^{-18}$	$0.547 \times 10^{-19}$

The above figures show how enormously the solution-tension may differ in different substances. For magnesium and zinc it is many millions of atmospheres, for copper, mercury (ous), and silver extremely small fractions of an atmosphere. The amount of sulphate which would have to dissolve in order to produce an osmotic pressure of the cations exactly as great as the solution-tension, is seen to vary between similar extremes; it is indicated in the last column of the table and was calculated from the equation  $PV = RT$ , in which  $P$  is taken as the solution-tension,  $V$  as the volume in which one equivalent of the metal must be present,  $R$  as the gas constant, and  $T$  as the absolute temperature. It is thus impossible to prepare a zinc solution concentrated enough to prevent the metal from driving zinc ions into the solution, while in the case of copper even an extremely dilute solution of one of its salts would be sufficient. Despite the comparatively large errors in the above data, due to the difficulty of determining the potential difference between the metal and its salt solution, the order of the decimal expressing the value of  $P$  can be accepted as reliable in each instance.

Some of these differences of potential are as follows:

Mg/MgSO <sub>4</sub>	= + 1.243 volts.
Zn/ZnSO <sub>4</sub>	= + 0.521 "
Cd/CdSO <sub>4</sub>	= + 0.158 "
Fe/FeSO <sub>4</sub>	= + 0.078 "
Pb/Pb acetate	= - 0.089 "
Cu/CuSO <sub>4</sub>	= - 0.582 "
Ag <sub>2</sub> /Ag <sub>2</sub> SO <sub>4</sub>	= - 1.024 "



The algebraic sign of these differences of potential can be directly determined from the solution-tensions. The electrolyte in which zinc is immersed must assume a positive potential and the metal itself a negative potential, because no zinc solution can be concentrated enough to hinder the emission of (positive) zinc ions by the metal. On the other hand, copper must become positive in respect to a copper solution, for even in the most dilute solutions the osmotic pressure of the copper ions is greater than the solution-tension of the metal.

**279.** A knowledge of the electrochemical series of the metals in electrolytes is of great practical value. Wherever combinations of various metals, alloys, metallic crustations, etc., are exposed to atmospheric action there is an opportunity to form cells of short circuit. In general, the metal with the greatest solution-tension goes into solution and the other remains intact. A piece of galvanized (zinc-plated) iron wire does not rust, even in those places where the plate has been worn off, as much as if it were not zinc-plated. The contrary phenomenon that tinned iron rusts faster than iron alone is also due to galvanic causes. If our hypothesis is correct the atmospheric moisture adhering to the metal must act as an electrolyte with the combination zinc-iron in such a way that iron becomes the dissolving (negative) electrode. Iron salts must therefore be formed and then transformed into rust by the loss of carbonic acid. The following experiment confirms this view. Rods of iron and tin are brought in contact by a wire which connects with a galvanometer. If the metals are dipped in water, into which air and carbonic acid are passed and to which is added a trace of sodium chloride (which always floats in the air and is washed down by the rain), the needle is deflected. The iron is found to be the anode and in the course of an hour a thin yellow coating of rust is to be observed on it. Sheet iron is tinned, as is well known, to prevent it from rusting (§ 199). If the tin plating is scratched off at any place so as to expose the iron, the latter begins to rust very rapidly, more so even than if it were not tinned. Galvanized iron, however, does not show a trace of rust where the plating has been damaged.

**280.** An ion can only go out of solution when a force greater than the solution-tension acts on it, just as electrically neutral molecules cannot crystallize out of a solution until its osmotic

pressure exceeds that of the saturated solution. The removal of an ion can be brought about by the action of an electrical force. This is the real principle of electrolysis. The separation of an ion from a solution thus requires a definite electromotive force, which must be equivalent to  $\frac{RT}{n} \ln \frac{P}{p}$  (see above) and must therefore be stronger as the solution-tension is greater and the osmotic pressure of the ions smaller. But since electrolysis takes place simultaneously at both the anode and the cathode, the total force  $E$  which is necessary for an electrolysis can be found by taking the sum of the forces necessary for the separation of the cation and the separation of the ion, thus:

$$E = E_1 + E_2 = \frac{RT}{n_1} \ln \frac{P_1}{p_1} + \frac{RT}{n_2} \ln \frac{P_2}{p_2}.$$

Since it is always the case that various sorts of anions and cations are present together in a solution, electrolysis can thus take place when  $E$  has become large enough to separate out one of the varieties of cations and one of the varieties of anions present.

This is the basis of a method of utilizing various electromotive forces to effect an **electrolytic separation of metals**. It is not the current strength which is of primary importance to the electrolytic process (as was formerly supposed), but the difference of potential between the electrodes. A very successful example of this method is the separation of copper from zinc. With a weak current it is possible to precipitate only the copper from a solution containing ions of both metals; if the current is strengthened, zinc also is separated.

In many cases the ions of the water are more easily separated than those of the dissolved electrolyte. In the electrolysis of potassium hydroxide, for example, OH-ions are liberated at the anode (they are at once decomposed, however, into water and oxygen); at the cathode it is not potassium ions but hydrogen ions (in spite of their extremely small concentration) which are discharged, since the solution-tension of hydrogen is much less than that of potassium.

281. The dissociation tensions  $E$  for various ions are given below. The figures are based on normal solutions.

$E_1$ (Cations).	$E_2$ (Anions)
Ag - 0.771	I' - 0.520
Cu - 0.329	Br' - 0.993
H 0.0	O'' - 1.08
Pb + 0.148	Cl' - 1.417
Ca + 0.420	OH' - 1.68
Zn 0.770	SO <sub>4</sub> '' - 1.9
	HSO <sub>4</sub> ' - 2.6

The dissociation tension of hydrogen is fixed at zero in the above table. Inasmuch as there is always an anode and a cathode, it is possible to subtract from all the values of  $E_1$  an arbitrary but constant amount and add it to the values of  $E_2$ , without affecting  $E = (E_1 + E_2)$ . The symbol O'' represents a secondary ionization product of the hydroxyl ion:



which, according to NERNST, we are obliged to assume, although only to an extremely small degree.

These figures lead us to important results. In the first place they enable us to know at once the dissociation tension of any combination of ions. Zinc bromide, for instance, will require  $0.993 + 0.770 = 1.763$  volts for its electrolysis; when the concentration of the ions is normal, the electrolysis of hydrochloric acid will require  $1.417 + 0 = 1.417$  volts, and so on. It is also obvious that it must be easy to separate silver from copper electrolytically, since the difference of their dissociation tensions is almost 0.5 volt. It also appears theoretically possible to separate electrolytically iodine from bromine and bromine from chlorine.

The order of the metals in the above electrochemical series is the same as that in which one metal is precipitated from its solution by the succeeding ones. As soon as a trace of the dissolved metal is deposited on the other one, the two metals form with the liquid an element, which electrolyzes the surrounding solution. The formula

$$E = \frac{RT}{n} \ln \frac{P}{p}$$

tells us, however, that the values of  $E$  depend not only on the solution tension but also on the osmotic pressure of the cations.

Very decided changes in the concentration of the salt solution would make the order of the metals a different one. For instance, it would be possible to conceive a case in which lead would not be precipitated by cadmium.

The electrochemical series of the anions also brings out important relations. Bromine must quickly liberate iodine from iodide solutions and chlorine quickly liberate bromine from bromide solutions because of the marked difference in their dissociation tensions. We see, further, that chlorine must be able to generate oxygen in acid solutions, but not so with bromine or iodine. It is also known, however, that the generation of oxygen by chlorine proceeds with extreme slowness, in sharp contrast to the rapidity with which chlorine deprives bromine of its negative charge:



This is not surprising in the light of the above considerations, for the chlorine, in order to enter the ionic condition, must make use of the ion  $\text{O}''$ , of which there is only an extremely small amount present. The hydroxyl ion  $\text{OH}'$ , which is present in relatively much larger amount and which after the loss of its negative charge would also yield a quantity of oxygen equal to that of the chlorine, holds its charge more than 0.3 volt firmer than the chlorine ion in acid solution.

The application of electrolysis to commercial processes is referred to in connection with the substances concerned (*cf.* §§ 223, 226, 242, 245, 248, and elsewhere).

## BORON.

**282.** This element occurs in nature as *borax*,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ aq}$ , and in boric acid,  $\text{H}_3\text{BO}_3$ . It can be obtained in the elemental state by the reduction of boric anhydride,  $\text{B}_2\text{O}_3$ , or borax by means of magnesium powder. The product is extracted with boiling water and hydrochloric acid and then treated with hydrofluoric acid or fused with borax. After another treatment with boiling water the pure element is left as a chestnut-brown amorphous powder having a specific gravity of 2.45. It is insoluble in the ordinary solvents and does not melt even in the electric arc.

It dissolves in molten aluminium and crystallizes out on cooling

in transparent, slightly colored crystals, having a lustre, refractive power and hardness not far below that of diamond. These crystals contain more or less aluminium and carbon as impurities. This crystallized modification is much less readily attacked by chemical agents than the amorphous variety.

Amorphous boron takes fire in fluorine and chlorine, uniting with them directly. When ignited in the air it burns to the oxide  $B_2O_3$ . At a very high temperature it combines with nitrogen to form boron nitride, BN. It reduces many compounds, such as CuO and PbO, and decomposes water at red-heat. Heating with nitric and sulphuric acids converts it into boric acid. It is also attacked by boiling caustic alkalies (like aluminium):



**Boron hydride.**—When boric anhydride is reduced with an excess of magnesium powder, *magnesium boride*,  $Mg_3B_2$ , is formed. The latter on being added to hydrochloric acid generates an ill-smelling gas consisting of hydrogen and a little boron hydride. This gas mixture burns with a green flame. By cooling with liquid air RAMSAY and HATFIELD obtained from it a gas  $B_3H_3$ ; probably the mixture also contained  $BH_3$ .

### Halogen Compounds.

**Boron chloride**,  $BCl_3$ , can be prepared by direct synthesis or by heating a mixture of boron trioxide and charcoal in a current of chlorine, that is, by the same process as that by which silicon chloride (§ 192) and aluminium chloride can be prepared. Boron chloride boils at  $17^\circ$ . Its vapor density indicates the above formula. Water breaks it up into hydrochloric and boric acids; it was with the aid of this reaction that the composition of the compound was determined.

**Boron fluoride**,  $BF_3$ , is formed, like silicon fluoride (§ 193), when the oxide is warmed with a mixture of calcium fluoride and sulphuric acid:



It is a gas, of which water dissolves 700–800 volumes. A solution of this concentration fumes in the air. On dilution boric acid

separates out after some time; *hydrofluoboric acid*,  $\text{HF} \cdot \text{BF}_3$ , is left in the solution. This acid cannot be isolated in the free state, but various salts of it are known. It thus displays a very close analogy to silicon fluoride.

### Oxygen Compounds of Boron.

**Boron oxide**,  $\text{B}_2\text{O}_3$ , boric anhydride, is obtained as a vitreous mass by igniting boric acid. It is very hygroscopic and is reconverted by the absorbed water into boric acid. With hydrofluoric acid it forms boron fluoride. The oxide is volatile only at elevated temperatures.

**283. Boric acid**,  $\text{H}_3\text{BO}_3$ , is found in the volcanic districts of Tuscany, where jets of steam (the springs are called "fumaroles" and the jets proper "*soffioni*") containing a little boric acid issue from the earth. The steam is conducted into water in which the boric acid is retained. When this liquid reaches a certain concentration, it is allowed to settle, whereupon it is piped off into a very long, flat leaden pan, which is warmed to about  $50\text{--}60^\circ$  by other *soffioni*. At this temperature the boric acid volatilizes but very little with steam and when the concentration has become great enough it crystallizes out. It is purified by converting it into borax, which is recrystallized and then decomposed by hydrochloric acid, setting free boric acid.

Boric acid crystallizes in lustrous laminae, which feel greasy and are difficultly soluble in cold water (about 3% at ordinary temperatures). This solution acts as a weak antiseptic, for which purpose it is frequently used. At  $100^\circ$  boric acid loses 1 molecule  $\text{H}_2\text{O}$ , passing over into **metaboric acid**,  $\text{HBO}_2$ . At  $140^\circ$  **tetraboric acid**,  $\text{H}_2\text{B}_4\text{O}_7$  ( $= 4\text{B}(\text{OH})_3 - 5\text{H}_2\text{O}$ ) is formed, the sodium salt of which is borax.

No salts of the normal boric acid,  $\text{B}(\text{OH})_3$ , are known but metaboric acid forms several. They are unstable and are converted by carbon dioxide into salts of tetraboric acid:



The best-known salt of boric acid is **borax**,  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ , often called *trinkal*. At present most of the borax on the market is made by boiling *colemanite*,  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{aq}$ , (found in California,)

with soda. Borax swells greatly on heating; this is due to the escape of water of crystallization from the semi-molten salt. On continued heating it forms a vitreous mass. This glass has the property of dissolving metallic oxides, some of which give double borates of a characteristic color; hence its use in qualitative analysis. The same property makes it valuable in soldering; solder adheres only to the untarnished metal, so a little borax is placed on the surface of the metal and heated with the soldering-iron in order to remove the rust. The dissolving of metallic oxides is easily understood, when we write  $\text{Na}_2\text{B}_4\text{O}_7$  as  $2\text{NaBO}_2 + \text{B}_2\text{O}_3$ ; it is the boric oxide,  $\text{B}_2\text{O}_3$ , which can be regarded as combining with the metallic oxides to form salts.

Boric acid is a weak acid; its salts are therefore hydrolyzed quite perceptibly—more so as the dilution increases. This can be illustrated by a simple experiment devised many years ago by ROSE. To a concentrated solution of borax some litmus is added and then acetic acid until the litmus is just red; if the liquid is then diluted, it turns blue because the alkali is set free and boric acid has scarcely any effect on litmus.

### ALUMINIUM.

284. This metal does not occur native, but in combination it is found in large quantities and very widely diffused. *Corundum*, including the precious stones *sapphire* and *oriental ruby* and the natural abrasive *emery* (all noted for their hardness), consists of alumina  $\text{Al}_2\text{O}_3$ , colored by traces of other oxides. *Bauxite* is a hydrate of aluminium and iron. *Clay* and *kaolin* (China clay) are principally aluminium silicate. Many other minerals, such as *feldspar*, *mica*, etc., contain it as a base. A peculiar aluminium mineral, *cryolite* or *ice stone*,  $3\text{NaF} \cdot \text{AlF}_3$ , is found in Greenland.

The metal can be obtained from the chloride by reduction with sodium but at present it is produced exclusively by decomposing aluminium oxide with the electric current.

The most important commercial process is that of HALL (invented independently in Europe by HEROULT). Alumina is dissolved in a fused bath consisting of cryolite or an equivalent mixture. The process is carried out in a large carbon-lined pot, the inner surface of which constitutes the cathode. Carbon rods immersed in the bath serve as the anode. Fresh alumina is added

from time to time and the metal is drawn off at the bottom periodically. The temperature is a little above the melting-point of eryolite. A current of several thousand amperes and less than 8 volts maintains the liquidity of the bath as well as effects the electrolysis.

The increased output due to improved methods has brought the price of the metal down from over \$90 per pound in 1856 to about \$0.30 in 1902, and the production is steadily increasing.

Aluminium is a silvery-white metal of low specific gravity (2.583). It is very ductile and malleable and fuses at about 700°.

It is permanent in the air, since it soon becomes coated with a firm thin layer of oxide. Small fragments burn with a bright light when heated in an oxygen atmosphere. It is not attacked by dilute nitric acid at ordinary temperatures and only slightly so by dilute sulphuric acid. Hydrochloric acid dissolves it readily, as does also caustic potash, hydrogen being evolved and *aluminates* formed in the latter case.

Before the efforts of DEVILLE to bring about its preparation on a large scale were rewarded (1850) and before its properties were well known, great expectations were centred in this "silver out of clay." It was thought that if it could be cheaply prepared, it would displace the other metals and even compete with iron. Although the metal can now be produced at a really low price, those expectations are far from being fulfilled. This is undoubtedly due in large measure to the properties of the metal; its softness, inability to stand heavy strains or to resist the action of alkalis (soap) and acetic acid greatly depreciates its supposed value. The cause of these disappointing facts lies partly, however, in slight impurities which are present in the commercial grades and seriously affect the properties of the metal. To this we may attribute the great difference of opinion in regard to its utility. A trace of nitrogen or carbon, for instance, greatly impairs its tensile strength; if traces of sodium are present, it is so readily attacked by water that the latter eats holes in sheets of the metal, although the pure metal is unaffected by water. However, aluminium bids fair to find extensive use in electrical work and lithography and for various purposes where lightness is important.

Various *alloys of aluminium* have also found a place in the arts. Among them mention may be made of *aluminium bronze*, which consists of copper and 5-12% aluminium. It can be easily cast and has a golden color and lustre. Its great firmness and elasticity render it valuable for physical instruments (balance beams) and watch springs. New alloys of aluminium are being constantly brought on the market: there is one with magnesium called *magnalium* and another with tungsten, for example.



Aluminium reduces many oxides (GOLDSCHMIDT) with a vigorous evolution of heat (§ 293). The reduction proceeds of itself after it has been started at a certain place in the mixture. For this purpose a primer is used consisting of a mixture of oxygen-producing substances, such as  $\text{KClO}_3$ , etc., and a piece of magnesium ribbon, which is ignited with a match. The heat that is thus evolved is used to heat iron bolts to white-heat and also for welding railroad rails, etc. The latter is accomplished by packing the rails in a mixture of iron oxide, sand, and aluminium powder together with a special sort of cement for making it compact. When this mass is ignited it continues to burn and heats the rails to glowing.

An *amalgam of aluminium* is easily prepared by introducing aluminium filings into a  $\frac{1}{2}\%$  solution of corrosive sublimate. This amalgam decomposes water energetically at ordinary temperatures, liberating hydrogen and forming aluminium hydroxide. As neither basic nor acid substances go into solution, it is a *neutral reducing agent*. The cause of this energetic reaction is due to the circumstance, that the mercury hinders the formation of a thin firm coating of oxide over the surface of the metal, which would otherwise protect it from further oxidation.

### Compounds of Aluminium.

**285.** The only known *oxide* of aluminium is **alumina**,  $\text{Al}_2\text{O}_3$ , which is formed on heating aluminium salts or the hydroxide. It is a white amorphous powder, readily soluble in acids; however, after it has been strongly ignited it is no longer soluble and must then be disintegrated by fusion with potassium hydroxide or acid potassium sulphate. It is found crystallized in nature (§ 284).

The ruby and the sapphire can be prepared artificially by fusing the amorphous  $\text{Al}_2\text{O}_3$  with lead oxide at bright red heat in a Hessian crucible. The silica of the crucible then acts on the lead aluminate,  $\text{PbO} \cdot \text{Al}_2\text{O}_3$ , primarily formed, setting free the alumina in beautiful crystals, exactly similar to the natural gems. The addition of a little potassium bichromate to the fused mass gives the crystals the same color as the active ruby; cobalt oxide produces sapphire.

**Aluminium hydroxide**,  $\text{Al}_2\text{O}_3 + n\text{H}_2\text{O}$ , is deposited as a hydrogel (§ 195) when a solution of an aluminium salt is treated with ammonia. In the decomposition of the aluminates it is obtained as a white powder. A hydrate with a low percentage of

water,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , *bauxite*, occurs in France and different parts of the United States in large deposits. Aluminium hydroxide is both weakly acidic and weakly basic in character. Its salts with acids suffer partial hydrolysis in aqueous solution and hence react acid (§ 239). It dissolves in alkalis to form *aluminates*, such as  $\text{AlO}_2\text{K}$ ,  $\text{AlO}_2\text{Na}$  and  $\text{AlO}_3\text{Na}_3$ , they are deposited in the amorphous state when alcohol is added to their aqueous solutions. They are decomposed by atmospheric carbonic acid.

Aluminium hydroxide is insoluble in water but dissolves in a solution of aluminium chloride. By subjecting this solution to dialysis, it is possible to get rid of the hydrochloric acid (which is present because of hydrolytic dissociation) entirely, and thus obtain a colloidal solution of the hydroxide. Aluminium hydroxide does not form salts with weak acids.

**Aluminium chloride**,  $\text{AlCl}_3$ , is most conveniently prepared by passing dry hydrochloric acid gas over aluminium filings in a tube of porcelain or glass and collecting the sublimed product in a wide-mouth bottle (see Fig. 80). After the tube has been heated

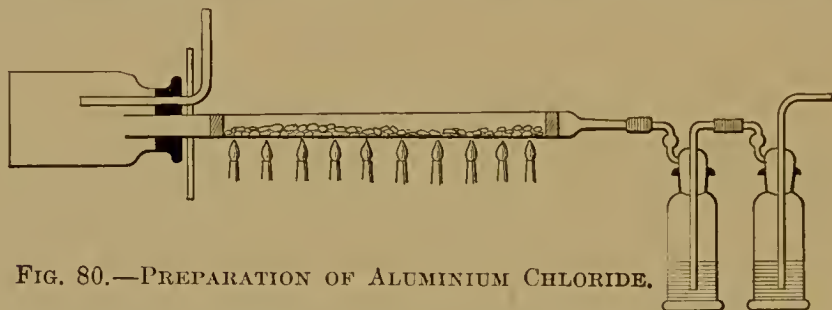


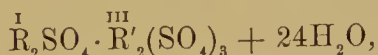
FIG. 80.—PREPARATION OF ALUMINIUM CHLORIDE.

to a sufficiently high temperature to start the reaction, no further heating is required; however, it is more practicable to continue heating in order to collect the chloride in the receiver.

Aluminium chloride is very hygroscopic. The aqueous solution hydrolyzes so readily, depositing alumina, that it can only be preserved by the addition of an excess of hydrochloric acid. Such a solution does not yield aluminium chloride on evaporation since it decomposes completely into the hydroxide and hydrochloric acid on account of the continued removal of the latter dissociation product. The vapor density of the chloride up to  $400^\circ$  corresponds to the formula  $\text{Al}_2\text{Cl}_6$ , above  $760^\circ$  to  $\text{AlCl}_3$ . With the chlorides of potassium and sodium, aluminium chloride forms

compounds such as  $\text{AlCl}_3 \cdot \text{KCl}$ , whose solutions can be evaporated without decomposition. Compounds such as  $\text{AlCl}_3 \cdot \text{PCl}_3$ ,  $\text{AlCl}_3 \cdot \text{POCl}_3$ , etc., have also been prepared. In organic chemistry anhydrous aluminium chloride is of great value in synthetical work.

**Aluminium sulphate**,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ , is obtained by treating clay with concentrated sulphuric acid; the product is dissolved in water and allowed to crystallize. Aluminium sulphate unites with the alkali salts to form double salts of the general type:



which are known as **alums**. R may be either K, Na,  $\text{NH}_4$ , Cs, Rb, Tl, or an organic base; R' may be Fe (ic) or Cr, instead of Al. The alums all crystallize in octahedrons and cubes, which often grow to large dimensions; they form mixed crystals readily. Ordinary alum (potassium alum) is used as a mordant in dyeing (Organ. Chem., § 357) but it is being gradually superseded as such by aluminium sulphate and sodium aluminate. In the vicinity of Rome the mineral *alunite*, or *alum stone*, is found, whose composition is  $\text{K}(\text{AlO}_2\text{H}_2)_3(\text{SO}_4)_2$ ; from it a much sought variety of alum is made. Alum is also made from cryolite, etc.

When two salts combine we may have either of two results: the new salt which is formed gives ions in dilute aqueous solution that differ from those of the two salts, or it gives the same ions. A good example of the former case is yellow prussiate of potash; it gives neither ferrous ions nor cyanide ions, so that it must be regarded as  $\text{K}_4(\text{FeCy}_6)$ . Such salts are termed **complex**. The second case is illustrated by the alums. A dilute alum solution exhibits all the reactions which characterize its components and its conductivity is the mean of the two separate salts for the same concentration. When the union is of this sort we have what is called a **double salt**. Between the two kinds there are salts of an intermediate nature which form not only complex ions but also the original ions to a greater or less extent. The copper-ammonia compounds (§ 244) behave in this way.

**286. Aluminium silicate**, *kaolin*, is formed in nature by the weathering of the numerous alkali-alumina double silicates, the alkali silicate being dissolved out leaving the insoluble aluminium silicate. Clay is aluminium silicate; it is usually colored brown by iron oxide. It is the essential raw material of the ceramic

industries, being used for rough bricks and the finest chinaware; of course the better grades require better sorts of clay. Bricks are molded out of ferruginous and calcareous clays (loam) and then baked ("burned," or "fired") till they become firm. Under the head of *earthenware*, or porous ware (faïence, majolica, etc., and common crockery) we understand all articles which consist of burned clay (frequently mixed with quartz), are porous and display an earthy fracture and which are covered with a glaze of easily fusible silicates. The glaze is produced by introducing salt into the kiln. The hot steam causes the formation of hydrochloric acid and sodium hydroxide, which unite with the clay to form sodium aluminium silicate. In *porcelain* the pores of the earthen mass are completely filled with fused silicate, as a result of the addition of feldspar and quartz before the burning. The less of such admixtures is present, the more difficult the porcelain is to burn and the less sensitive it is to changes of temperature.

Clay is the most widely diffused refractory material; it resists not only high temperatures and sudden changes of temperature, but chemical action as well.

*Ultramarine* is a very beautiful blue pigment, which is prepared artificially by heating a mixture of clay, soda, sulphur and wood charcoal in the absence of air. It occurs in nature as *lapis lazuli*. It is usually regarded as a compound of sodium aluminium silicate with polysulphides of sodium. This is indicated by the fact that it is attacked by acids with the evolution of hydrogen sulphide, and the disappearance of the color, while it is unaffected by alkalies. It is still uncertain what substance gives the pigment its blue color.

#### GALLIUM, INDIUM, THALLIUM.

287. The existence of gallium was predicted by MENDELÉEFF (§ 217) in the same manner as that of germanium. The hypothetical *eka-aluminium* was discovered in 1875 by LECOQ DE BOISBAUDRAN in a zinc blende by means of spectral analysis. Its spectrum consists of two violet lines. It is a very rare element. The metal is white, melts as low as 30° and has a specific gravity of 5.9. It is only superficially oxidized by the air and is not attacked by water. Like aluminium it is only slightly affected by nitric acid but dissolves readily in hydrochloric acid as well as ammonia and potassium hydroxide. It forms alloys with aluminium, which, when the proportion of aluminium is small, are liquid at ordinary temperatures because of the melting-point depression of gallium, and decomposes water almost as readily as sodium.

In its compounds, also, gallium displays much analogy with aluminium.

The **hydroxide** dissolves in alkalis; the **chloride**,  $\text{GaCl}_3$ , fumes in the air like  $\text{AlCl}_3$  and the solution yields hydrochloric acid on evaporation. **Gallium sulphate** gives an **alum**,  $\text{Ga}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 + 24\text{H}_2\text{O}$ , with ammonium sulphate. Hydrogen sulphide precipitates gallium only from an acetic acid solution, in which respect gallium resembles zinc (§ 269).

**Indium** has already been referred to in the discussion of the periodic system (§ 216), so that it will be passed over here with a few words. It was discovered through its spectrum, a blue line. This element, too, occurs very rarely, being found in certain blendes. The **metal** is white; m.-pt.,  $176^\circ$ ; sp. g., 7.42. It is permanent in the air; heated to a high temperature it burns with a blue flame to the **oxide**,  $\text{In}_2\text{O}_3$ . The **chloride**  $\text{InCl}_3$  is hygroscopic; its aqueous solution does not decompose on evaporation. The **sulphate** forms an alum with ammonium sulphate. The **hydroxide** dissolves in alkalis.

288. **Thallium** is the most common of these three elements, notwithstanding it always occurs in limited amounts. It is occasionally found in the *Abraum salts* carnallite and sylvite and frequently also in different native sulphides. When the zinc blendes are roasted in sulphuric acid factories the thallium goes off with the fumes and settles in the flue dust and chamber mud. From these deposits it is obtained by boiling with dilute sulphuric acid and precipitating with hydrochloric (or better hydriodic) acid, whereupon the sparingly soluble  $\text{TlCl}$  (TlI) is deposited. This element was also discovered with the spectroscope (CROOKES); its spectrum is a bright green line.

Thallium is a soft metal, about like sodium, and has a bluish color like lead. Sp. g., 11.8; m.-pt.,  $290^\circ$ . In moist air it oxidizes very rapidly at the surface; but it does not decompose water at ordinary temperatures. When heated it burns with a beautiful green flame. Sulphuric and nitric acids dissolve it readily but hydrochloric acid acts very slowly because of the slight solubility of the chloride.

There are two sets of compounds: the *thallous* compounds, derived from the oxide  $\text{Tl}_2\text{O}$ , and the *thallic* compounds, from the oxide  $\text{Tl}_2\text{O}_3$ . The former resemble those of the alkalis and silver very much. This similarity shows itself, for instance, in the solubility of the hydroxide and of the carbonate, whose solutions react alkaline. Moreover many thallium salts are isomorphous with potassium salts and, like the latter, give double salts with platinum chloride, e.g.,  $\text{Tl}_2\text{PtCl}_6$ . Farther there is an alum  $\text{Tl}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  as well as other double sulphates, e.g.,  $\text{Tl}_2\text{SO}_4 \cdot \text{MgSO}_4 + 6\text{H}_2\text{O}$ , which are analogous to the corresponding potassium double salts. On the other hand thallium resembles silver and lead in the small solubility of its halides (the iodide is the least, and the chloride the most, soluble), also in respect to the order of solubility of these compounds.

In the thallic compounds the element is trivalent like the others of the group; moreover, like the latter, they readily form complex salts, and undergo considerable hydrolysis when dissolved in water.

## Summary of the Group.

289. The five elements last considered, B, Al, Ga, In, Tl, form a natural group, in which the last three display particular similarity to each other in their physical properties. Something analogous was observed with copper, silver and gold in the first group and with zinc, cadmium and mercury in the second group. The following table affords a brief comparison of certain physical data.

	B	Al	Ga	In	Tl
Atomic weight . . . . .	11	27.1	70	113	204.1
Specific gravity . . . . .	2.45	2.58	5.9	7.4	11.8
Melting-point . . . . .	very high	700°	30°	176°	290°

Of the spectra of Ga, In and Tl it is again noticeable that the lines move towards the red end as the atomic weight increases (§ 265).

As to their chemical nature it may be remarked that all the elements of this group are trivalent and that the basicity of their oxides increases with rising atomic weight; boron hydroxide (boric acid) has exclusively acid properties, but the hydroxides of the other elements, even  $Tl(OH)_3$ , are also soluble in alkalis. As most of the lower oxides of the metals are more strongly basic than the higher oxides, it is not strange that thallous hydrate is a strong base.

## THE RARE EARTHS.

290. In the middle of the periodic table (p. 284) are located a number of elements, which are classed under the term "rare earths." There is still much uncertainty in regard to some of them, particularly as to their homogeneity, i.e., as to whether they are elements or mixtures. This is due in large measure to the great similarity between the elements and the consequent difficulty of separating them. The following are now accepted as elements: scandium (Sc), yttrium (Y), lanthanum (La), ytterbium (Yb), cerium (Ce), erbium (Er), praseodymium (Pr), neodymium (Nd) and samarium (Sm); we may also mention terbium, thulium and holmium (the last three are not included in the table of atomic weights, see p. 34).

These elements occur in various rare minerals which have been found principally in Sweden and Greenland, viz., *cerite*, *gadolinite*, *euxenite*, *orthite*, etc.

Since the use of the oxides of cerium and thorium in the incandescent gas-light of AUER VON WELSBACH has created a demand for them, minerals in which the rare earths occur are being ardently sought. The interesting fact has developed that they are by no means so "rare" as was supposed. An especially rich source of these earths has been found in *monazite sand*, which occurs in quite large quantities in the United States (production in 1900 908,000 lbs.), Canada and Brazil. It consists chiefly of a phosphate of Ca, La, Di, Y and Er with variable amounts of thorium silicate and thorium phosphate.

In order to isolate the rare earths from these minerals the latter are powdered very finely and heated to faint-red heat with concentrated sulphuric acid. Thus the rare earths are changed into sulphates and the silicic acid converted into the insoluble condition. The sulphates are then taken up in ice-water, in which they dissolve much more readily than in warm water (since a difficultly soluble hydrate is formed at a higher temperature). From this cold solution they can be precipitated with oxalic acid, their oxalates being almost insoluble even in dilute acids. Thus they are freed from Ca, Fe, etc. The oxalates are then converted into oxides by heating.

The separation of these oxides is a more difficult task. Various methods are in use. The insolubility of the sulphates of cerium, lanthanum and didymium in a saturated sodium sulphate solution (by reason of the formation of double salts) is made use of to separate them from erbium, ytterbium and yttrium. The nitrates of the various metals of this group differ markedly in their stability on heating; hence another method of separation has been devised, by which nitrates are decomposed one after another by heating and those that remain undecomposed after each successive heating are extracted with water. A third method is the fractional precipitation of the solutions with ammonia. Farther, by fractional precipitation with potassium chromate (the insoluble neutral chromates being deposited) separations can be accomplished which are otherwise very difficult. An important aid in these separations is the fact that the solutions of some of these metals (both didymium metals, erbium, samarium, etc.) give absorption spectra; it is thus possible to detect whether the separation is complete.

Some of the rare earths which have been more carefully studied will be described here briefly.

Cerium occurs principally in *cerite* (as high as 60%). Its salts are colorless when pure and give no absorption spectrum (§ 263). To separate cerium oxide (ceria) from the oxides of lanthanum and didymium (the latter is a mixture of Pr and Nd) these oxides are warmed with an aqueous solution of chromium trioxide till all has dissolved. The resulting solution is then evaporated to dryness and heated to 110° for some time. Cerium chromate is thus decomposed, yielding ceria,  $Ce_2O_3$ . If the mass is then

extracted with water, the chromates of lanthanum and didymium go into solution leaving the insoluble ceria. Another method is to treat the solution with ammonium persulphate, when cerium only is precipitated as a basic ceric salt.

The metal looks like iron and is quite permanent in the air. At an elevated temperature it takes fire. It forms two sets of salts, the *cerous salts*, which can be derived from the oxide  $Ce_2O_3$  and are colorless, and the *ceric salts*, derivable from  $CeO_2$ , which are yellow or brown. Cerium is thus quadrivalent (as the existence of the fluoride  $CeF_4 + H_2O$  also indicates) and so belongs to the fourth group of the periodic system. When chlorine is passed into an alkaline solution of a cerous salt a yellow precipitate of  $CeO_2$  is obtained.

Lanthanum can be separated from didymium by adding to their solution sodium hydroxide until the liquid no longer gives an absorption spectrum (see above). The precipitate then contains the didymium metals and a little lanthanum, but the liquid is free from the former. Lanthanum is only trivalent. Its oxide  $La_2O_3$  and its salts are colorless when pure.

*Didymium* was formerly regarded as an element but AUER VON WELSBACH succeeded in splitting it up into two components, called *praseodymium* and *neodymium*. This can be accomplished by making use of the difference in solubility of their potassium double sulphates in a concentrated solution of potassium sulphate. The praseodymium salts are green and give green solutions; the neodymium salts have an amethyst color and give pink solutions. The absorption spectra of the two elements differ considerably.

Scandium is likewise a trivalent element. Its existence was predicted by MENDELÉEFF, who called it *ekaboron*. Its trivalence places it in the aluminium group. Its hydrate  $Sc(OH)_3$  is gelatinous but insoluble in an excess of alkali.

**Ytterbium.**—The oxide  $Yb_2O_3$  is the main constituent of *erbia* (obtained from *euxenite* and *gadolinite*), which also contains the oxides of scandium, yttrium, erbium, etc. Ytterbia (oxide) is obtained by fractional heating of the nitrate mixture (see above). The salts of ytterbium are colorless and give no absorption spectrum.

The salts of **samarium** are yellow and have a characteristic absorption spectrum.

#### TITANIUM, ZIRCONIUM AND THORIUM.

**291.** These uncommon elements are related to carbon and silicon in the same way as K, Rb and Cs are to Li and Na, and as Ca, Sr and Ba are to Be and Mg. Titanium and zirconium still give acid-forming oxides, while thorium only forms basic oxides.

**Titanium** displays very close analogy to silicon; it frequently occurs with the latter but always in a small amount. The element can be obtained by reduction of the oxide with aluminium. It is white, very hard and extremely refractory. Sp. g. 4.87. **Titanium dioxide**,  $TiO_2$ , occurs in



three modifications: *rutile*, *anatase* and *brookite*. Titanium chloride,  $\text{TiCl}_4$ , is prepared by passing chlorine over a glowing mixture of charcoal and  $\text{TiO}_2$ . It is liquid and fumes in the air because of decomposition by atmospheric water into  $\text{HCl}$  and  $\text{Ti}(\text{OH})_4$ . Titanic acid,  $\text{Ti}(\text{OH})_4$ , separates out as a white amorphous powder when the hydrochloric acid solution of a titanate is treated with ammonia. This action is due to the weak basic character of ammonia and the weak acid nature of titanac acid; as a result the ammonium titanate is completely hydrolyzed (§ 239). Like silicic and stannic acids, titanac acid readily forms poly-acids (§ 195). It dissolves in alkalis to form titanates, which are also obtained by fusing  $\text{TiO}_2$  with alkalis. On the other hand titanac acid dissolves in concentrated sulphuric acid; it then remains in solution even when poured into water, because the excess of sulphuric acid hinders hydrolytic dissociation. Higher as well as lower oxides of titanium are known. The lemon-yellow oxide  $\text{TiO}_2$  is formed on treating the sulphuric acid solution of  $\text{Ti}(\text{OH})_4$  with  $\text{H}_2\text{O}_2$  (§ 38).

Zirconium occurs in nature chiefly as *zircon*,  $\text{ZrSiO}_4$ . MOISSAN obtained zirconium carbide,  $\text{CZr}$ , from this mineral directly by heating it together with sugar charcoal vigorously in an electric furnace (1000 amp. and 40 volts) for ten minutes. The silicon volatilizes for the most part. If the carbide is treated with chlorine at dark-red heat, it is converted into the chloride. Zirconium chloride behaves with water in the same way as  $\text{TiCl}_4$  and  $\text{SnCl}_4$ . The hydroxide,  $\text{Zr}(\text{OH})_4$  is precipitated by ammonia from acid solutions as a voluminous mass. It is insoluble in alkalis but on being fused with the latter forms salts such as  $\text{Na}_2\text{ZrO}_3$  and  $\text{Na}_4\text{ZrO}_4$ , which are decomposable by water. The basic character of the hydroxide is apparent from the fact that it gives a sulphate,  $\text{Zr}(\text{SO}_4)_2$ , with sulphuric acid, which can be recrystallized out of water. *Zirconia*,  $\text{ZrO}_2$ , emits a very bright light when heated strongly and can therefore be used advantageously instead of lime in the DRUMMOND light (§ 13).

Thorium is at present obtained mainly from monazite sand; it is also found in the *thorite* of Arendal. The hydroxide  $\text{Th}(\text{OH})_4$  is insoluble in alkalis. The sulphate crystallizes with  $9\text{H}_2\text{O}$ .

Thoria and ceria are the essential constituents of the *incandescent gas light* of A. VON WELSBACH. A finely woven cotton "mantle" is saturated with a solution of the nitrates of thorium and cerium, in which the two are contained in such a proportion that after ignition the ash contains 98-99% thoria and 2-1% ceria. When this ashen mantle is heated to incandescence by a Bunsen burner it gives out an intense light. This is apparently due to the fact that such an ash-mantle emits only a small proportion of red rays and rays of still greater wave length but mainly gives out rays of shorter wave length; hence, very little, if any energy is lost by the emission of rays giving little light. However it is found that a mantle consisting of thoria or ceria alone or of the two oxides in a proportion different from the above produces very little light. So far as the ceria is concerned

this is due to its being present in such an excess that it cannot all be raised by the flame to full incandescence. An analogous phenomenon is seen in an ordinary flame, which when smoking (i.e., when too much carbon is present) gives less light than one which does not smoke. That it is not the thoria which emits the light is proved by the fact that a mantle consisting chiefly of ceria and containing only 1–2% of thoria produces very little light. We must therefore suppose that in the mantles minute particles of ceria are spread out upon the very poor heat-conductor, thoria; thus since their mass is small they are able to reach the high temperature at which they emit the desired bright light; for the brightness of a flame increases with about the fifth power of the temperature.

In the *incandescent electric light* of NERNST the incandescent body ("glower") has the form of a wire rod, prepared from a mixture of rare earths (Zr, Th, Yt, Ce, etc.) and glazed. Both ends of the rod are connected with the wires conveying the current. At ordinary temperatures the rod is a non-conductor but if it is warmed (by a burning match, e.g.) a current begins to pass through (if the potential is high enough) in gradually increasing amount; this heats the glower still higher so that in a short time it reaches bright incandescence. The interesting feature of this lamp is that a substance which is a non-conductor at ordinary temperatures becomes a conductor at a higher temperature. In its more recent form the NERNST lamp is supplied with an automatic electric "heater" close to the wire, so that no "lighting" is required. By reason of its efficiency this lamp bids fair to rival the arc-light. According to NERNST, the "glower" conducts the electricity by an electrolytic process and not like a metal. One of the grounds for this belief is the fact that a metal conducts the electric current worse as the temperature rises, but that electrolytes behave in the opposite way.

#### VANADIUM, NIOBIUM (Columbium), TANTALUM.

292. These very rare elements are allied to nitrogen and phosphorus in their properties and the formulæ of their compounds; as is the case in all other groups the metallic character becomes more prominent as the atomic weight increases.

**Vanadium**, which occurs in certain iron ores and in *vanadinite*, a lead vanadate, is characterized by an abundance of compound-types. There are, for example, four chlorides:  $VCl_2$ ,  $VCl_3$ ,  $VCl_4$  and  $VCl_5$ . An oxychloride,  $VOCl_3$ , also is known, which is decomposed by water like  $POCl_3$ . The highest oxide,  $V_2O_5$ , a brown substance, is an acid anhydride; it forms salts which may be derived from the acids  $H_2VO_4$  (ortho-acid) and  $HVO_3$ , metavanadic acid, and is thus analogous to  $P_2O_5$ .

An important salt is the *ammonium metavanadate*,  $NH_4VO_3$ ; it is insoluble in ammonium chloride solution, which property is valuable in separating vanadium from its ores. The latter are fused with caustic soda and saltpetre, producing sodium vanadate, which is extracted with water.

On saturating this solution with ammonium chloride,  $\text{NH}_4\text{VO}_3$  separates out after a while as a sandy powder. Heating converts it into  $\text{V}_2\text{O}_5$ . This also serves as the characteristic test for vanadic acid.

Vanadium is finding various uses, both as the brown oxide and in alloys. Moreover it is much less rare than was supposed, for traces of it occur in many granitic and other rocks.

Niobium (frequently called *columbium*) and tantalum form volatile chlorides,  $\text{NbCl}_5$  and  $\text{TaCl}_5$ , which (like  $\text{PCl}_5$ ) are decomposed by water. Particularly characteristic of these elements are their double fluorides,  $2\text{KF} \cdot \text{NbOF}_3$ , and  $2\text{KF} \cdot \text{TaF}_5$ . The latter is difficultly soluble, the former readily soluble, in water. Use is made of these compounds in separating the two elements. The oxides  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  in the presence of bases form salts of niobic acid,  $\text{H}_3\text{NbO}_4$ , and tantalic acid,  $\text{H}_3\text{TaO}_4$ . The element niobium is obtained in the free state by heating niobic acid with sugar-coal in the electric furnace. It then contains about 3% of carbon. As it is not attacked by acids, it resembles boron or silicon more than the metals.

## CHROMIUM GROUP.

### Chromium.

293. This element occurs principally in *chromite*,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  (§ 294), and less commonly in *crocoite*,  $\text{PbCrO}_4$ . The former serves exclusively for the preparation of chromium compounds; for this purpose it is very finely powdered and fused with an alkali, thus forming chromates, which are extracted with water.

The element has been known for a long time but it was not until 1894 that it was prepared pure on a large scale by MOISSAN. He reduced chromium oxide,  $\text{Cr}_2\text{O}_3$ , with charcoal in the electric furnace. An easier method is that of GOLDSCHMIDT (§ 284), by which chromium oxide is reduced with aluminium filings. If care is taken to have an excess of chromium oxide present, the metal is obtained entirely free from aluminium.

The metal thus obtained is lustrous and takes a polish. It does not melt in the oxyhydrogen flame but is completely liquefied in the electric furnace. It does not scratch glass (although the carbide  $\text{C}_2\text{Cr}_3$  scratches quartz and topaz). At ordinary temperatures its behavior is that of a precious metal, i.e., it is entirely unaffected by the air. OSTWALD has observed a very remarkable phenomenon in dissolving chromium in dilute acids, viz., that the evolution of hydrogen is periodic; after a few minutes of vigorous gas evolution there is a cessation for a few minutes. Not all

pieces of chromium metal show this peculiarity. It is not yet clear what causes this periodicity.

According to HITTORF'S researches the metal chromium appears in two wholly different modifications. The metal obtained by the GOLDSCHMIDT method is not attacked by dilute hydrochloric or sulphuric acid at ordinary temperatures. It is *inactive*. On being heated with one of these acids, however, it begins to generate hydrogen vigorously, chromous chloride going into solution. The metal has thus entered the *active* condition, for the evolution of hydrogen continues on cooling to room temperature and also recommences after the metal has been removed, rinsed off and introduced into cold dilute hydrochloric acid. If a bar of chromium in a solution of this sort is connected by a wire with some platinum foil in a silver nitrate solution and the two liquids are connected with each other by a concentrated solution of saltpetre, a galvanic cell is obtained with an E. M. F. of 1.8 volts. Active chromium thus stands between cadmium and zinc in the electrochemical series. On the other hand, if inactive chromium is combined with platinum in the same manner, the E. M. F. only reaches 0.3 volt. Between these two extreme, or limiting, conditions of the metal there are various intermediate forms. The inactive form is more stable than the active. Either modification can be obtained at will by the following process: If the active metal in contact with hydrochloric acid is made the anode of a more powerful current, the hydrogen evolution ceases at once and yellow scales of chromic acid are soon observed to fall from the surface of the metal; the metal has become inactive. If thereupon the current is reversed (making chromium the cathode), a vigorous evolution of hydrogen begins at the surface of the metal. On breaking the circuit the gas continues to come off, although at a much slower rate. The metal is restored to the active condition. It might seem reasonable to ascribe the inactivity of chromium simply to the fact that, when exposed to the air or to other oxidizing agents, or when serving as anode, it becomes coated with an extremely thin film of oxide, which protects it from further rusting. Many of the above facts could indeed be well explained by this supposition, e.g., the conversion of the metal into the active condition on warming with dilute hydrochloric acid. But warming with solutions of alkali halides also renders chromium active. This is one of the facts which makes the existence of two conditions more likely.

Chromium forms three sets of compounds, derived from  $\text{CrO}$  *chromous oxide*,  $\text{Cr}_2\text{O}_3$  *chromic oxide* and  $\text{CrO}_3$  *chromic anhydride*.

#### CHROMOUS COMPOUNDS.

These compounds have a very great tendency to absorb oxygen and go over into chromic compounds; hence they can only be pre-

served away from the air. A solution of the **chromous chloride**,  $\text{CrCl}_2$ , is obtained by reducing chromic chloride,  $\text{Cr}_2\text{Cl}_6$ , with zinc and sulphuric acid. It has a beautiful blue color, which soon turns to green because of oxidation. If the solution of chromous chloride is poured into a saturated solution of sodium acetate, **chromous acetate** is precipitated as a red crystalline powder, which is much more permanent in the air than the other chromium salts and can therefore be used for their preparation. The **hydroxide**  $\text{Cr}(\text{OH})_2$  is yellow.

#### CHROMIC COMPOUNDS.

**294. Chromic oxide**,  $\text{Cr}_2\text{O}_3$ , is formed by heating chromic anhydride,  $\text{CrO}_3$ , or ammonium chromate (§ 105). It can be obtained crystallized by passing chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , through a red-hot tube. The amorphous compound is green, the crystals are black. After ignition it is insoluble in acids. When fused with silicates it colors the latter green, whence its use as a pigment for coloring glass and chinaware (*chrome green*).

GUIGNET'S *green*, a beautiful pigment, is prepared by fusing potassium bichromate (1 part) with boric acid (3 parts). The potassium borate is dissolved out with water leaving the coloring substance,  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .

The *hydrate of chromic oxide*,  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , is precipitated when a chromium salt is treated with ammonia. It is light blue but dissolves in caustic potash or soda to a green solution. On boiling this solution a lower hydrate of another color is deposited. The formation of this lower hydrate explains the cause of the precipitation, if it is assumed that its saturated solution contains less chromium ions than that of the higher hydrate. The alkaline solution is thus supersaturated in respect to the lower hydrate and the latter must be deposited. The solubility of chromic hydroxide in alkalis shows its slightly acidic character; it can also form salts with other metals, most of which salts derive themselves from  $\text{CrO} \cdot \text{OH}$ . An example of this sort is the mineral *chromite*.

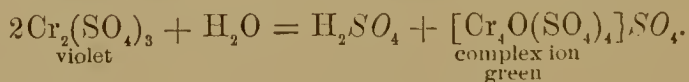
Chromium hydroxide is only a weak base; it does not form salts with weak acids such as carbonic acid, sulphurous acid, etc. (*cf.* § 239).

**Chromium chloride**,  $\text{CrCl}_3$ , is prepared by heating a mixture of chromic oxide and carbon in a current of chlorine; it then sublimes in brilliant violet crystal-laminae. Chromic chloride thus

obtained dissolves in cold water very slowly, but, if traces of chromous chloride are present, it dissolves readily. According to OSTWALD, this is to be regarded as a catalytic acceleration of the velocity of solution. The resulting solution is green; on evaporation green deliquescent crystals of the composition  $\text{Cr}_2\text{Cl}_6 + 12\text{H}_2\text{O}$  separate out. These crystals are also obtained from the solution of the hydrogel in hydrochloric acid. At  $1200\text{--}1300^\circ$  the vapor density corresponds to the formula  $\text{CrCl}_3$ .

**Chromic sulphate**,  $\text{Cr}_2(\text{SO}_4)_3$ , like other chromium salts (nitrate, chrome alum, etc.), has the peculiar property of dissolving in cold water to a violet solution, which turns green on warming. On cooling, this green color changes back to violet (rather slowly with the sulphate solution but rapidly with other salts). On slowly evaporating the violet solution at room temperature the salts crystallize out, the sulphate for instance, with  $15\text{H}_2\text{O}$ ; the green solution, however, yields only an amorphous viscid mass.

In investigating these phenomena the sulphate solution has been usually employed, since its green modification can be kept the longest. Experiments have shown that the process depends on a splitting off of sulphuric acid (1 mol.  $\text{H}_2\text{SO}_4$  from 2 mols. sulphate) and that green "chrom-sulphuric acids" are formed, i.e., substances with a complex chrom-sulphuric acid ion, since they do not give tests for either chromium or sulphuric acid. Thus only one-third of the sulphuric acid can be precipitated from a green solution of the sulphate directly with barium chloride, or in other words, only a third of the  $\text{SO}_4$  ions of the original violet solution are still present. The transition from the violet solution to the green can therefore be formulated in this way:



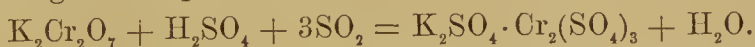
Only those  $\text{SO}_4$  groups in italics are precipitated.

In a moderate state of dilution these chrom-sulphuric acids are just as strongly ionized as sulphuric acid itself.

An analogous behavior is shown by chromic chloride,  $\text{CrCl}_3$ . A violet solution of it can be obtained by treating the violet solution of the sulphate with the theoretical amount of barium chloride. The chlorine can then be completely precipitated with silver nitrate at ordinary temperatures. If the solution is boiled

for a time, however, and then cooled, silver nitrate will precipitate only two of the three chlorine atoms directly under the same conditions; the third must have gone with chromium to form a complex ion.

**Chrome alum**,  $K_2SO_4 \cdot Cr_2(SO_4)_3 + 24H_2O$ , is best prepared by passing sulphur dioxide into a solution of potassium bichromate containing free sulphuric acid:



It can be obtained in finely developed octahedrons with edges several centimetres in length. It is used in dyeing and tanning.

#### CHROMATES.

**295.** There are numerous salts of the formula  $M_2CrO_4$  which are derived from the oxide  $CrO_3$ , chromic anhydride, as in the similar case of sulphuric anhydride,  $SO_3$ ; but while in the latter case the sulphuric acid itself,  $H_2SO_4$ , is also a stable compound, chromic acid,  $H_2CrO_4$ , has not as yet been isolated. When an acid is added to a chromate only the anhydride is obtained; the acid  $H_2CrO_4$  breaks up forthwith into water and anhydride. The salts of chromic acid are isomorphous with the corresponding sulphates.

**Chromic anhydride** is obtained on adding sulphuric acid to a concentrated solution of potassium bichromate; it separates out in the form of long red rhombic needles, which, when freed from all sulphuric acid, do not deliquesce in the air. They are readily soluble in water. Heating to  $250^\circ$  breaks them up into chromic oxide and oxygen:



Chromium trioxide is a very powerful oxidizing agent; its solution cannot be filtered through paper because the latter is destroyed by oxidation. When strong alcohol is dropped on chromic anhydride it takes fire, chromic oxide ( $Cr_2O_3$ ) being formed at the same time. Hydrochloric acid is oxidized to chlorine and water, sulphurous acid to sulphuric acid. On passing dry ammonia over  $CrO_3$  crystals, the gas takes fire and the oxide is reduced. When heated with sulphuric acid it yields oxygen and chromium sulphate. Hydrogen sulphide reduces the aqueous solution, sulphur being deposited. Chromic anhydride

thus displays various characteristics of peroxides such as  $\text{PbO}_2$ ,  $\text{BaO}_2$ , etc.

In addition to the normal salts of chromic acid, e.g.,  $\text{K}_2\text{CrO}_4$ , there are also bichromates, trichromates, etc., which can be regarded as combinations of one molecule of the neutral salt with one or more  $\text{CrO}_3$  molecules:



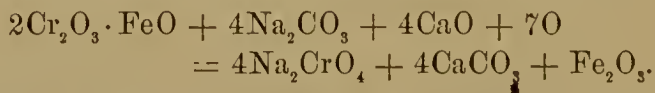
If  $\frac{1}{2}$  molecule of sulphuric acid is added to 1 molecule of chromate, the yellow color of the chromate solution is changed to the red color of the bichromate; a  $\text{CrO}_4$  ion gives up its electrical charge and an atom of oxygen to the hydrogen ions of the free acid, thus yielding water and forming, together with a second  $\text{CrO}_4$  ion, the red ion  $\text{Cr}_2\text{O}_7$ :



Acid salts of chromic acid do not exist on account of this reducing effect of the hydrogen ions on the  $\text{CrO}_4$  ions.

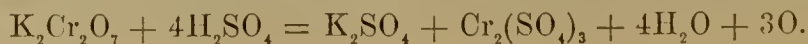
Chromic acid is a weak acid, since its insoluble (in water) salts, e.g., those of barium, lead and silver, are readily dissolved by strong acids (§ 146).

**Alkali chromates** are invariably obtained by fusing a chromium compound with an alkali carbonate and an oxidizing agent. The latter is unnecessary when the fused mass can be brought sufficiently in contact with the oxygen of the air by stirring. Chromite is worked up commercially into chromates in this way; it is calcined in a reverberatory furnace with soda and lime:



The resulting sodium chromate is lixiviated and sulphuric acid is added to its solution; on evaporation **sodium bichromate**,  $\text{Na}_2\text{Cr}_2\text{O}_7$ , crystallizes out, and this can be converted into **potassium bichromate**, a well-known salt, by double decomposition with potassium chloride.

Potassium bichromate finds frequent use as an oxidizing agent in sulphuric acid solution, being itself reduced to chromic sulphate:

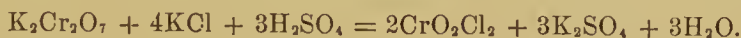




An important commercial task is the regeneration of the chromic acid from such a chromium sulphate solution. The method followed in the factories at Höchst, Germany, is an electrical one. The solution is electrolyzed between lead electrodes in a vessel containing a diaphragm (porous partition). By the action of the current chromic acid is formed at the anode, while at the cathode hydrogen is evolved. Besides this, a change occurs in the concentration of the sulphuric acid on both sides of the diaphragm; it becomes higher in the anode portion, and lower in the cathode portion. The liquid oxidized at the anode can be used for oxidizing purposes without any further preparation. The chromic acid is again reduced to chromic oxide,  $\text{Cr}_2\text{O}_3$ , and the reduced liquid is then introduced into the cathode-space, while the liquid which previously occupied that space, is brought over to the anode side of the diaphragm. When the current is again turned on, the liquid at the cathode, which at the beginning of this second operation is richer in sulphuric acid than the liquid at the anode, yields its surplus to the cathode liquid. In this way an accumulation of sulphuric acid is avoided, and the same liquid can really be used continuously as an oxidizing-agent.

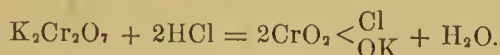
The chromates are yellow (except silver chromate, which is red) and the bichromates are red. Lead chromate,  $\text{PbCrO}_4$ , is insoluble in water and is used as a pigment (*chrome yellow*).

On heating potassium bichromate with potassium chloride and sulphuric acid a dark red liquid distills over, which has the composition  $\text{CrO}_2\text{Cl}_2$  and the boiling-point  $117^\circ$  and must be considered as the chloride of chromic acid; it is called **chromyl chloride**, or chromium oxychloride:



Water breaks it up into  $\text{CrO}_3$  and  $\text{HCl}$ .

The semi-chloride of chromic acid,  $\text{CrO}_2 \left\langle \begin{smallmatrix} \text{Cl} \\ \text{OH} \end{smallmatrix} \right.$ , is known only in the form of salts. The potassium salt, for example, is obtained by heating potassium dichromate with concentrated hydrochloric acid:



It crystallizes in red prisms.

On treating a chromic acid solution with hydrogen peroxide in excess a beautiful blue coloration appears, which is absorbed by shaking with ether. It is due to a **perchromic acid**, whose ammonium salt  $\text{NH}_4\text{CrO}_5 + \text{H}_2\text{O}_2$  can be isolated as a violet-black powder similar to powdered potassium permanganate. In concentrated aqueous solution decomposition soon occurs, the bichromate being formed and oxygen given off.

## Molybdenum.

296. This comparatively rare element is found in nature in *molybdenite*,  $\text{MoS}_2$ , and *wulfenite*,  $\text{PbMoO}_4$ . The former is used exclusively in preparing molybdenum and its compounds. It is roasted and so converted into the trioxide,  $\text{MoO}_3$ .

The element itself is obtained from its oxides or chlorides by heating them red-hot in a current of hydrogen. The product is a steel-gray powder which fuses with great difficulty to a silvery metallic mass. Sp. g. = 8.6. Heating in the air converts it into the trioxide. It is not attacked by hydrochloric or dilute sulphuric acid but is readily dissolved by nitric and concentrated sulphuric acids.

Molybdenum is noted for the great variety of its compounds; some of these may be mentioned here.

In addition to the oxides  $\text{Mo}_2\text{O}_3$  (weakly basic) and  $\text{MoO}_2$  (indifferent) there is **molybdenum trioxide**,  $\text{MoO}_3$ , which, like  $\text{CrO}_3$ , is an acid anhydride. It is a white powder which turns yellow on heating. It is very sparingly soluble in water. With alkalis it forms *molybdates*. It has a tendency to form *poly-molybdates* even stronger than the similar tendency of chromic anhydride; ammonium heptamolybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + 4\text{H}_2\text{O}$  (derivable from the acid  $7\text{H}_2\text{MoO}_4 - 4\text{H}_2\text{O}$ ), for example, and many others are known. The addition of a strong acid to a molybdate solution precipitates white, glistening crystal-laminae of **molybdic acid**,  $\text{H}_2\text{MoO}_4$ , which dissolve in an excess of acid. A solution thus prepared from ammonium molybdate and an excess of nitric acid serves as a test-reagent for phosphoric acid, with which it forms a yellow precipitate of about the composition  $(\text{NH}_4)_3\text{PO}_4 \cdot 14\text{MoO}_3 + 4\text{H}_2\text{O}$  on warming (*cf.* §§ 146 and 162).

Of the chlorides an  $\text{MoCl}_3$ , an  $\text{MoCl}_4$ , and an  $\text{MoCl}_5$  are known. In the oxychlorides  $\text{MoOCl}_4$  and  $\text{MoO}_2\text{Cl}_2$  molybdenum can be regarded as hexivalent.

The chloride  $\text{MoCl}_2$  does not exist according to MUTHMANN (neither does  $\text{MoO}$ ), but a chloride  $\text{Mo}_3\text{Cl}_6$  is known.

A very *characteristic test* for *molybdic acid* (the most common molybdenum compound) is the following: the substance is mixed with zinc and sulphuric acid; at first a blue coloration (a molybdate of molybdic oxide) appears but it soon turns green and then brown. This brown coloration is due to a salt of the oxide  $\text{Mo}_2\text{O}_7$ .

## TUNGSTEN.

297. The minerals in which this element chiefly occurs are *scheelite*,  $\text{CaWO}_4$ , *wolframite*, or *wolfram*,  $(\text{Fe}, \text{Mn})\text{WO}_4$ , and *hübnerite*,  $\text{MnWO}_4$ . The metal is obtained pure by the method of GOLDSCHMIDT (§ 284), i.e. by the reduction of pure tungstic acid with aluminium filings. The temperature thus produced is not high enough, however, to convert the metal into a regulus, or matte. STAVENHAGEN raised the temperature very considerably by adding liquid air to the reduction mixture before ignition; under these conditions the separate particles of tungsten unite to form a fused regulus. The metal so obtained is very pure; sp. g. 16.6. It is malleable and scratches glass. In combination with carbon it is very much harder. It is very permanent in the air. Sulphuric acid, hydrochloric acid, aqua regia, and hydrofluoric acid attack it very slowly, but it rapidly dissolves in a mixture of hydrofluoric and nitric acids. Fused caustic potash dissolves it slowly with the evolution of hydrogen. Tungsten is employed in the iron industry, since a small percentage of tungsten increases the hardness of steel in a marked degree (*tungsten*, or *wolfram*, *steel*).

Tungsten, like chromium and molybdenum, is also characterized by an abundance of compound types. The chlorides  $\text{WCl}_2$ ,  $\text{WCl}_4$ ,  $\text{WCl}_5$ , and  $\text{WCl}_6$  are known to exist. The lower ones are prepared from the hexachloride by heating in a current of hydrogen or carbon dioxide. The hexachloride itself is formed by direct synthesis; it is a violet-black crystalline substance; water converts it into the anhydride,  $\text{WO}_3$ .

Tungstic anhydride,  $\text{WO}_3$ , is obtained by precipitating the hot solution of a tungstate with nitric acid. It is insoluble in water and acids but soluble in alkalies. The addition of an acid to the cold solution of a tungstate precipitates tungstic acid,  $\text{WO}(\text{OH})_4$  [ $= \text{W}(\text{OH})_6 - \text{H}_2\text{O}$ ]. The latter forms polyacids, like chromic and molybdic acids. Like the latter acid it also has the property of uniting with phosphoric and arsenic acids to form complex phospho-tungstates and arseni-tungstates. The following is a very characteristic test for tungstates: If stannous chloride is added to a tungstate solution, a yellow precipitate ( $\text{WO}_3$ ) is produced. On the addition of hydrochloric acid and warming, a beautiful blue solution ( $\text{W}_2\text{O}_6$ ) is obtained.

## URANIUM.

298. The principal uranium mineral is *uraninite*,  $\text{U}_3\text{O}_8$ , which usually contains some iron. The metal is obtained by heating the chloride with sodium or by the electrolysis of the chloride or by the reduction of the oxide with carbon in the electric furnace. It is silvery white and has a specific gravity of 18.7. It is much more volatile than iron in the electric furnace. When it is in the form of a fine powder it burns in a current of oxygen as low as  $170^\circ$ . In the same state it decomposes water slowly at room temperature. When nitrogen is passed over uranium the two ele-

ments combine readily at  $1000^{\circ}$  to form a yellow nitride. Another interesting compound is the carbide  $C_3U_2$  (obtained from uranium oxide and charcoals in the electric furnace), inasmuch as the addition of water yields not only methane but liquid and solid hydrocarbons.

Uranium forms two sets of compounds; in the *ous* compounds it is quadrivalent ( $UX_4$ ), in the *ic* compounds hexivalent ( $UX_6$ ). The former pass readily into the latter. The oxide  $UO_2$  has an exclusively basic character; it is obtained by igniting the other oxides in a current of hydrogen. It was at one time regarded as the metal itself.

**Uranic oxide**,  $UO_3$ , is a yellow powder, prepared by heating the nitrate. The corresponding hydroxide,  $U(OH)_6$ , is not known, but salts of the compound  $U(OH)_6 - 2H_2O = UO_2(OH)_2$  with acids have been prepared. Since the  $UO_2$  group acts here as a bivalent radical it is called *uranyl* and its salts uranyl salts, e.g.  $UO_2(NO_3)_2$  **uranyl nitrate**, crystallizing with  $6H_2O$  in beautiful greenish-yellow prisms. Uranium trioxide also has somewhat the character of an acid anhydride; if caustic potash and soda are added to uranyl salt solutions yellow *uranates* ( $K_2U_2O_7$  and  $Na_2U_2O_7$ ) are precipitated, which are soluble in acids. Uraninite can be regarded as the uranate of uranous oxide,  $U_3O_8 = 2UO_3 \cdot UO_2$ . Both oxides are converted into this  $U_3O_8$  oxide by heating in the air. Uranium salts are used to impart to glass a beautiful greenish-yellow fluorescence.

The *detection of uranyl salts* is accomplished with the aid of the precipitate, soluble in excess, which they give with ammonium carbonate and by the reddish-brown precipitate with potassium ferrocyanide.

#### RADIUM, POLONIUM AND ACTINIUM.

BEQUEREL has discovered that *uraninite* emits a peculiar sort of rays. They move in a straight line and act on a photographic plate; but they cannot be reflected or refracted or polarized. When they pass through gases the latter become electrical conductors. It was for a while a question whether these properties belonged to uranium or to substances mixed with it in the uraninite. This mineral is very complex, containing besides  $U_3O_8$  as the principal constituent, a whole series of other metallic compounds. It is chiefly the merit of M. and Mme. CURIE to have proved that the emission of these particular rays, or the *radio-activity*, is due to the presence of very minute quantities of three elements, hitherto unknown, which they have called radium, polonium and actinium.

In order to separate these elements from the uraninite residues, left after the extraction of uranium, their only guide was to measure the radio-activity of the products obtained in each operation; this was done by measuring the conductivity of an air-layer, exposed to the rays. They thus succeeded in concentrating the active substance more and more by numerous chemical operations. This method is quite comparable to that followed by BUNSEN and KIRCHHOFF in the extraction of rubidium and caesium from

the Dürkheim mineral water, in which the spectroscope indicated whether a concentration of these elements was effected. However, the measurement of the radio-activity is many thousand times more sensitive than spectroscopic observations.

**Polonium** is a substance which is found in company with the bismuth extracted from uraninite; its chemical properties are very much like those of that element. It can be isolated by the sublimation of bismuth sulphide *in vacuo*, since the active sulphide is the more volatile. As yet it has only been possible to obtain it mixed with much bismuth.

**Radium** is obtained nearly pure as chloride. It accompanies the baryta extracted from uraninite, and is separated from it by fractional crystallization of the chlorides, the chloride of radium being less soluble than that of barium.

**Actinium** has much analogy with thorium, from which it has not yet been separated. The quantity of these elements occurring in uraninite is very slight; in order to obtain a few centigrams of nearly pure radium chloride, 2000 kg. of uraninite residues had to be worked up.

Radium is the best studied of these elements. It has a characteristic spectrum, resembling that of the alkaline earths. Its atomic weight has not yet been accurately determined for lack of material, but it is above 174 (atomic weight of Ba = 137.4). Preparations of radium give light in the dark; when they are very concentrated, they transform oxygen into ozone in a marked degree and have an odor like *eau de Javelle* (§ 56). Under the influence of these rays glass assumes a brown color and potassium chloride and sodium chloride turn blue. For additional physical properties of the radioactive rays reference must be made to textbooks on physics.

### Summary of the Group.

299. The elements *chromium, molybdenum, tungsten, and uranium*, in connection with sulphur, constitute a natural group in the periodic system. Particularly in the higher oxides there is considerable analogy with the behavior of this metalloid. Their acids, for example, all have the formula  $H_2RO_4$ . Moreover sulphur also has the ability to form polyacids (pyrosulphuric acid) although it is not so prominent as in the first named four elements. Several of their salts are isomorphous. The strength of the acids decreases, as in other groups, with rising atomic weight. Another characteristic of all the elements of this group is the great abundance of formula-types; it is also very noticeable in the case of sulphur, whose acids are remarkably numerous.

## MANGANESE.

**300.** This element is widely diffused in nature. The most important minerals are *pyrolusite*,  $\text{MnO}_2$ , *hausmannite*,  $\text{Mn}_3\text{O}_4$ , and *rhodochrosite*,  $\text{MnCO}_3$ .

The metal is of minor importance. It is best prepared by the GOLDSCHMIDT method, i.e., by reducing pyrolusite with aluminium powder, when it is obtained as a regulus of brilliant lustre. Sp. g. = 7.2–8.0. It undergoes surface oxidation readily in moist air, which gives the regulus an iridescence, and when finely divided decomposes boiling water. It dissolves in acids to form manganous salts.

Manganese forms several series of compounds: the *manganous* compounds of the type  $\text{MnX}_2$ ; the *manganic* compounds,  $\text{MnX}_3$ ; *manganic acid*,  $\text{H}_2\text{MnO}_4$ , which can be derived from an anhydride  $\text{MnO}_3$ ; *permanganic acid*,  $\text{HMnO}_4$ , from the oxide  $\text{Mn}_2\text{O}_7$ . Most of the familiar salts of this element are derived from **manganous oxide**,  $\text{MnO}$ . This oxide, which is prepared by heating the carbonate in the absence of air, is an amorphous green powder, that oxidizes readily in the air to the higher oxide  $\text{Mn}_3\text{O}_4$ . **Manganous hydroxide**,  $\text{Mn}(\text{OH})_2$ , is white when freshly precipitated from solutions by an alkali but soon turns brown in the air because of the formation of manganic hydroxide,  $\text{Mn}_2(\text{OH})_6$ .

The solutions of **manganous** salts are pink (color of the  $\text{Mn}^{++}$  ion). The **chloride**,  $\text{MnCl}_2$ , crystallizes with four molecules of water. It can be obtained anhydrous by heating the double salt  $\text{MnCl}_2 \cdot 2\text{NH}_4\text{Cl} + \text{H}_2\text{O}$ , since the hydrochloric acid set free hinders the hydrolytic dissociation of the chloride. The **sulphate**,  $\text{MnSO}_4$ , crystallizes below  $6^\circ$  with  $7\text{H}_2\text{O}$ , above this temperature with  $5\text{H}_2\text{O}$ . It forms double salts, such as  $\text{K}_2\text{SO}_4 \cdot \text{MnSO}_4 + 6\text{aq}$ , similar to those of magnesium and iron; they are moreover isomorphous with the latter.

**Manganous sulphide**,  $\text{MnS}$ , has a pinkish-white color, which distinguishes it from all other sulphides. If ammonium chloride is added to the solution of a manganese salt, no hydroxide is precipitated by ammonia; this is analogous to what is observed with magnesium (§ 254). The solution is, however, readily oxi-

dized by the oxygen of the air and brown manganic hydroxide is deposited.

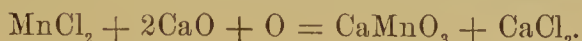
The manganic ion  $Mn^{+++}$  is only weakly basic. Its salts are almost completely hydrolyzed in aqueous solution. The sulphate gives alums with cerium and rubidium sulphates, which are also very unstable.

Manganic oxide,  $Mn_2O_3$ , is obtained from all of the other oxides by heating in an oxygen current. Since dilute sulphuric acid reacts with it, giving manganous sulphate and manganese dioxide, the oxide,  $Mn_2O_3$ , is often considered as  $MnO \cdot MnO_2$ . The corresponding hydroxide is soluble in cold hydrochloric acid to a dark-brown solution. It is not certain whether this solution contains  $Mn_2Cl_6$  or  $MnCl_2$  and  $MnCl_4$ ; on being warmed it gives off chlorine and is then known to contain the manganous chloride.

Mangano-manganic oxide,  $Mn_3O_4$  or  $MnO \cdot Mn_2O_3$ , is obtained by strongly igniting the other oxides in the air. It is a brownish-red powder. When heated with hydrochloric acid it yields chlorine.

Manganese di- (or per-) oxide,  $MnO_2$ , the best-known manganese mineral (*pyrolusite*), is commercially of great importance in the production of chlorine. In the cold it dissolves in hydrochloric acid to a very dark liquid, probably containing the tetrachloride, and gives off no chlorine; when warmed, it decomposes into chlorine and manganous chloride (§ 25).

Since pyrolusite is comparatively expensive, various methods have been devised for reconverting the manganous chloride into the peroxide. One which is of practical importance is the WELDON process. An excess of milk of lime is added to the chloride solution, whereupon air is forced through the warmed liquid. The manganous hydroxide which is precipitated undergoes oxidation and is converted into calcium manganite,  $CaMnO_3$  ( $= CaO \cdot MnO_2$ ), which settles as a black slimy mass:



The calcium chloride solution is run off and the manganite is used for generating chlorine, since it acts towards hydrochloric acid like a mixture of lime and manganese dioxide.

The value of the peroxide is based on the amount of chlorine it can produce with hydrochloric acid. In order to determine this the mineral, finely pulverized, is warmed with hydrochloric acid

and the evolved chlorine passed into potassium iodide solution, whereupon an equivalent amount of iodine is liberated. This iodine can be titrated with thiosulphate (§ 93).

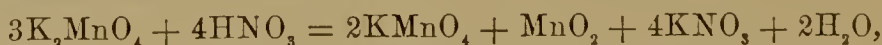
### Manganic acid and Permanganic acid.

301. When manganese compounds are fused with potassium hydroxide in the air or better in the presence of an oxidizing agent (potassium nitrate or chlorate) a green mass results which is dissolved by cold water forming a dark-green solution. On evaporating this solution in a vacuum dark-green rhombic prisms of **potassium manganate**,  $K_2MnO_4$ , crystallize out, which have a metallic lustre and are isomorphous with potassium chromate. They dissolve in potassium or sodium hydroxide solutions without any action but are decomposed by water with the separation of manganese dioxide and the formation of **potassium permanganate**,  $KMnO_4$ , the latter giving the solution a deep violet color.

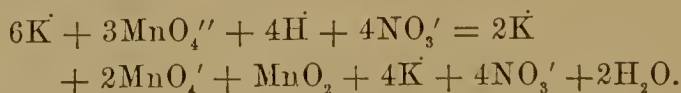


On account of these changes of color the manganate solution received the name of "mineral chameleon" from the early chemists.

Both in the solution of a manganate and in that of a permanganate we have the anion  $MnO_4$ ; in the former, however, it is bivalent, in the latter univalent. This causes the difference in the properties of the two ions; the univalent ion  $MnO_4'$  is deep red and resembles the perchloric acid ion in behavior, while the bivalent  $MnO_4''$  is deep green and displays analogy to the  $SO_4''$  ion of sulphuric acid. The bivalent  $MnO_4''$  is only stable in alkaline liquids; it is converted by water (more easily by acids) into the univalent ion:



or, written in ions:



The reaction obviously amounts to a formation of water by the four hydrogen ions and two oxygen atoms which they extract from a bivalent anion  $MnO_4''$ , the latter being reduced to  $MnO_2$ . Of the four negative charges which are required to neutralize the four



positive charges of the hydrogen ions two are taken from this  $\text{MnO}_4$  anion, which is reduced to  $\text{MnO}_2$ , and the remaining two from two other bivalent anions  $\text{MnO}_4''$ , which thus become univalent. The transformation of potassium manganate into the permanganate is effected commercially by passing ozone into its concentrated solution:



Permanganate crystallizes out of the solution and the resulting mother-liquor can at once be used with a fresh quantity of pyrolusite.

Potassium permanganate,  $\text{KMnO}_4$ , crystallizes in beautiful glistening greenish-black prisms of the rhombic system, which dissolve readily in water, forming a deep violet liquid. This salt is isomorphous with potassium perchlorate. All solutions of permanganates display the same absorption spectrum, viz., five dark bands in the yellow and green, no matter what the base is. It is thus manifest that it is really the ion  $\text{MnO}_4'$  that is the coloring-agent.

The solution of potassium permanganate acts as a powerful oxidizing-agent; in acid solutions two molecules  $\text{KMnO}_4$  yield five oxygen atoms:



The process may be regarded as a transformation of the anhydride of permanganic acid,  $\text{Mn}_2\text{O}_7 (= 2\text{HMnO}_4 - \text{H}_2\text{O})$ , into two molecules of basic oxide,  $\text{MnO}$ , and five atoms of oxygen; thus:  $\text{Mn}_2\text{O}_7 = 2\text{MnO} + 5\text{O}$ .

In neutral or alkaline solutions, however, two molecules  $\text{KMnO}_4$  yield only three atoms of oxygen, manganese peroxide being deposited at the same time (transformation of  $\text{Mn}_2\text{O}_7$  into  $2\text{MnO}_2 + 3\text{O}$ ):



Since in oxidations with potassium permanganate in acid solution the deep color of the permanganate is replaced by the very faint color of manganous sulphate, many substances can be titrated with potassium permanganate in acid solution without an indicator. Ferrous sulphate is oxidized to ferric sulphate; oxalic

acid gives carbon dioxide and water; nitrous acid in very dilute solutions is converted into nitric acid (§ 126); from hydrogen peroxide water and oxygen gas are produced. All these reactions proceed quickly and quantitatively at ordinary temperatures so that they are suitable for titration.

Manganese occupies an isolated position in the periodic system. No elements are known which are related to it as the elements Mo, W and U are to chromium. Moreover only in its highest stage of oxidation, permanganic acid, does it display analogy with the corresponding chlorine compound,  $\text{HClO}_4$ . The salts of both acids are isomorphous and both are powerful oxidizing agents.

## IRON.

**302.** Iron is the most useful metal and is therefore prepared commercially on an enormous scale. It occurs only rarely *native*, e.g. in meteoric rocks. In the form of oxides, sulphides and silicates it is widely diffused in nature and is found in very large quantities. The most important minerals for the iron industry are *magnetite*,  $\text{Fe}_3\text{O}_4$ , *hematite*,  $\text{Fe}_2\text{O}_3$ , and *siderite*,  $\text{FeCO}_3$ . The *pyrites* ( $\text{FeS}_2$ , etc.) are worked up into iron after they have been roasted in the sulphuric acid factories.

The **metallurgy** of iron is theoretically very simple; it is based on the ability of carbon to reduce the oxides of iron to the metal at an elevated temperature. This process (smelting) is carried out in *blast furnaces* (Figs. 81 and 82).

The iron ore is first roasted (calcined) to remove volatile substances ( $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , S, As, etc.) and loosen up the mineral. Then it is crushed and mixed with a slag-forming substance (*flux*, see § 242), according to the grade of the ore. If the gangue, or earthy matrix, contains much silica or alumina, limestone or dolomite is employed as the fluxing agent, but ores rich in lime or magnesia are mixed with quartz or aluminous ore to effect the necessary fusion and formation of slag (silicates of Al, Mg, and Ca).

The blast furnace, previously warmed to the proper temperature or already in operation, is charged from above with alternate layers of coke and the mixture of ore and flux, both being introduced in "rounds," or "charges," of definite weight. (Sometimes

charcoal or anthracite are used as fuel.) The modern furnaces (Fig. 81) are built of fire-brick encased in iron and are of much lighter construction than the older ones (Fig. 82). They vary

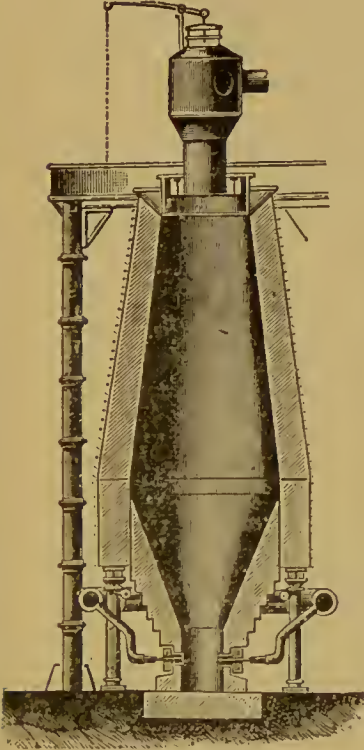


FIG. 81.  
MODERN BLAST FURNACE.

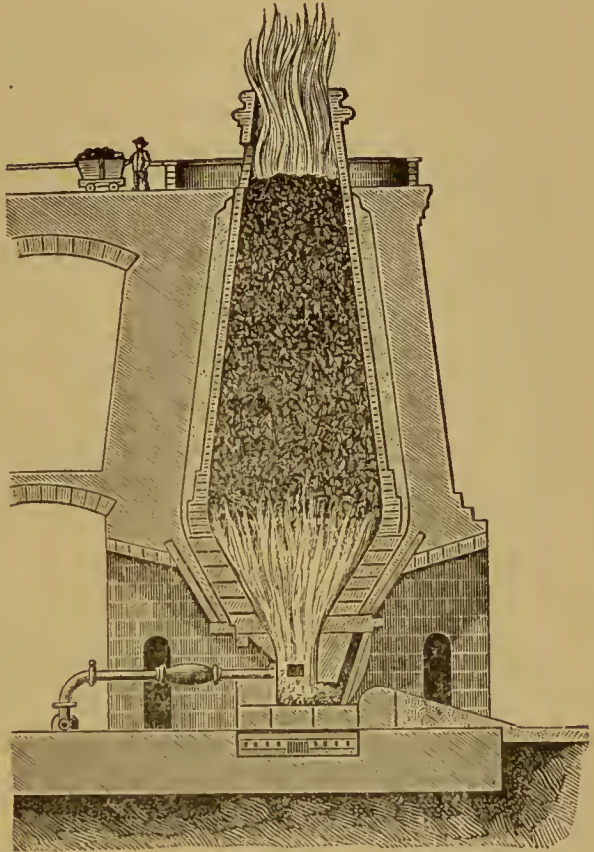


FIG. 82.  
OLDER TYPE OF BLAST FURNACE.

greatly in size but consist mainly of a long shaft tapering towards both ends. In order to utilize the escaping hot gases (CO, etc.) an apparatus ("cup and cone") is fitted on the top to conduct them off and also allow the introduction of the charge. The air necessary for the process is forced in hot through pipes (*twyers*) at the bottom of the furnace. The burning coke produces carbon monoxide, which is the principal factor in the reduction of the ore:

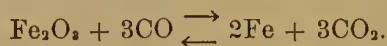


The reduced iron sinks downward and comes in contact with carbon at a high temperature; as a result some of the carbon

is dissolved by it and its melting-point considerably depressed. When a definite stage is reached the fused iron is drawn off below. It is protected from atmospheric oxidation by the slag floating on it.

**303.** It was stated above that the waste furnace-gases contain carbon monoxide, and in considerable quantity; therefore a large amount of heat is lost, which could be utilized by burning the monoxide to dioxide. Supposing that this incomplete reaction was due to an incomplete contact of carbon monoxide and ferric oxide, manufacturers increased the dimensions of the blast furnaces, particularly in England and America, a height of thirty meters being not uncommon. The ratio of carbon monoxide to the dioxide in the escaping gases was not affected however; it was thus demonstrated by very expensive experience that the reduction of ferric oxide by carbon monoxide has a limit. A study of the laws of chemical equilibrium would have led to this conclusion much more quickly and above all much less expensively. These laws teach us that:

1. In the reduction of ferric oxide by carbon monoxide an equilibrium is established between this action and the oxidation of iron by carbon dioxide.



2. The ratio  $\text{CO} : \text{CO}_2$  must be independent of the pressure, since no change in the volume of the gas takes place (§ 51).

3. This ratio varies only slightly with the temperature, since very little heat is generated in the reaction.

An experimental investigation conducted at a few different temperatures and pressures would have sufficed to determine the ratio  $\text{CO} : \text{CO}_2$ . The result, when compared with the ratio  $\text{CO} : \text{CO}_2$  of the waste gases, would thus have shown that little could be gained by an increase of the furnace dimensions. This illustrates in a very striking way the value of physical chemistry for industrial processes.

Efforts are now being made to utilize the waste gases in other ways, such as by burning them under the boilers of steam engines or in wind heaters (for heating the blast air, or "wind"). In recent years it has been found that greater efficiency is attained by using the hot waste gases directly in gas engines for motive-power.

**304.** The properties of iron are influenced in great measure by the slight admixtures which it contains, particularly by the carbon. The percentage of carbon forms the ordinary basis of classification of the different grades of iron under the heads, pig iron and malleable iron; however, in the industrial world this classification is not always adhered to.

**Pig iron**, or **cast iron**, contains 2.3–5.1% carbon. It fuses very easily but there is no previous softening; hence it is not malleable. It is brittle. This is the direct product of the blast furnaces and is therefore mixed with small amounts of silicon, phosphorus, sulphur, etc. The presence of manganese makes it coarsely crystalline and it is then known as *spiegel-eisen*. This is utilized mainly for steel.

**Malleable iron**, containing less than 2.3% carbon, is harder to fuse but is extensible and malleable and the more so the less the impurities. If the carbon amounts to 2.3–0.5%, the iron can be hardened; in this manner *steel* is obtained. If there is less than 0.5% carbon, it can no longer be hardened; this is *wrought iron*. It is obvious that between these main varieties there are numerous intermediate sorts, which are prepared in such a way as to suit the purpose for which they are intended.

Small admixtures of other elements have an equally great effect on the properties of iron. The presence of *silicon* has about the same effect as that of carbon, but it is less intense. *Sulphur* even in a small amount renders the iron brittle when hot and therefore useless for forging. On this account sulphurous ores as such are unsuitable for the manufacture of iron. *Phosphorus* makes the iron brittle at ordinary temperatures. It should also be mentioned that as a general rule the effect of these admixtures is strongly modified by the presence of others.

**305.** From the crude pig iron, the direct product of the blast furnace, the other varieties of iron are prepared. For this purpose it must be freed from silicon, sulphur, phosphorus, etc., as well as from a large portion of its carbon. The most important process for accomplishing this commercially is the **BESSEMER process**. The pig iron is fused and run into a pear-shaped apparatus (*converter*, Fig. 83), in the bottom of which there are holes ( $xx_1$ ) for blowing in air. Thus by the oxidation of silicon, manganese and a little iron and without the use of fuel the temperature is raised high enough to effect the burning of the carbon. The Bessemer process is easier controlled if the elimination of carbon is continued past the steel stage and until molten wrought iron is formed, whereupon enough carboniferous iron is added to furnish the desired percentage of carbon. At the completion of the process the converter is emptied by tipping.

An objection to the Bessemer process in its original form was that the phosphorus was not removed. The small amount of phosphorus present in iron might indeed be burned but the large

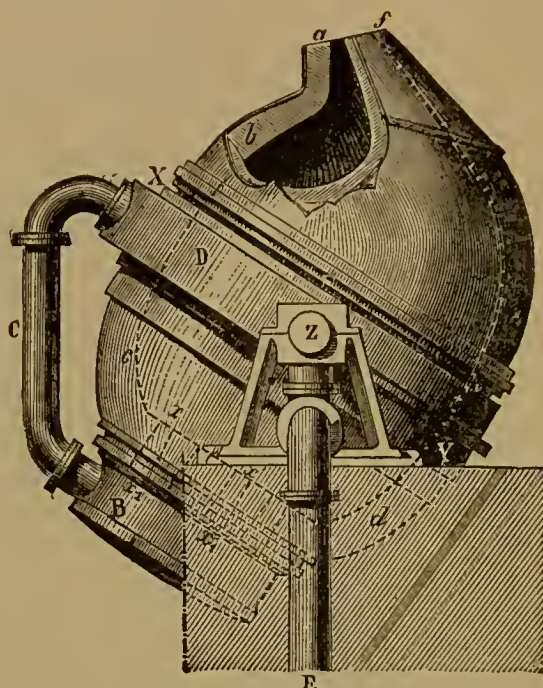


FIG. 83.—CONVERTER.

amount of molten iron would at once reduce it back to phosphorus or to iron phosphide. This fault was corrected by an improvement devised by THOMAS and GILCHRIST. The interior lining (*a b c d*, Fig. 83) consisted originally of nothing but refractory materials (ganister), rich in silica. This *acid* lining was replaced by them with a *basic* lining, consisting of clay and silica mixed with lime and magnesia and, in addition, lime was thrown into the converter with the pig iron. The phosphorus pentoxide produced by the combustion unites with the lime and magnesia and the phosphates are no longer reduced by the molten iron. As a side product a slag (*Thomas slag*) is thus obtained consisting of a basic phosphate, which is found to have great value as a fertilizer when ground very finely. It is brought on the market in enormous quantities.

The only successful rival of the Bessemer process is the SIEMENS, or *open-hearth process*. By employing a special furnace and gaseous fuel a mixture of cast iron and wrought iron (together with some iron ore) in the

proper proportions can be fused together so as to produce a very good steel. A basic lining can also be used with this process.

The production of wrought iron from pig iron is usually accomplished by the *puddling process*. Pig iron is melted in a reverberatory furnace lined with iron ore (oxide); the carbon and also the silicon are oxidized (and so removed) partly by the action of the air, but mainly by that of the ore, which is stirred in with the metal. The violent reaction due to escaping CO gives the process the name of "pig-boiling." The iron is then allowed to become pasty, when it is worked up into large masses (*blooms*), which are removed and hammered and rolled. The cinder is thus squeezed out and the iron is formed into bars.

Efforts have been made to enhance certain properties of steel which are valuable for particular purposes, by adding small amounts of other metals. A few of the results may be mentioned. The maximum hardness of steel is reached when it contains 1–2% carbon. If, however, some manganese (up to 8%) or chromium (up to 1%) is added, a much harder modification of steel is produced. The addition of nickel or aluminium makes wrought iron more malleable and elastic; as high as 3% nickel is sometimes added. The toughness of nickel steel makes it especially valuable for armor plate. Tungsten (*cf.* § 297) and molybdenum are also added for different purposes.

Further, the mode of manufacture can have great influence on the properties of iron. Steel, for instance, becomes very hard and brittle when it is suddenly cooled from a high temperature. If, however, it is then heated for a definite period and allowed to cool slowly, it becomes more or less *tempered* according to the temperature, i.e. it can be made to have any desired hardness and elasticity (within certain limits).

*Chemically pure iron* is obtained by reducing the oxide or chloride in a current of hydrogen. If the reduction takes place at a low temperature, the resulting iron powder is pyrophoric (§ 203). It is a silvery white, lustrous metal of the specific gravity 7.84, and does not melt below 1600°. It is the most magnetic of the metals; pure iron and wrought iron can be magnetized only temporarily, steel, however, permanently. Iron is permanent in dry air or in water free from air (CO<sub>2</sub>). In moist air it rusts rapidly (§ 279), forming ferric hydrate; as the rust does not form a compact film it keeps on forming.

The rusting of iron is greatly retarded by contact with water containing a little alkali or salts of alkaline reaction. In a soda solution, for

instance, iron remains bright. The rusting of iron in contact with water can be explained by assuming that the oxygen dissolved in water endeavors to form hydroxyl ions with the hydrogen ions. In order to compensate their negative potential the iron sends its positive ions into the solution; in a short time the solubility product of ferric hydrate is reached and the latter is deposited; in other words, the iron rusts.

Now, if hydroxyl ions are previously introduced into the liquid by the addition of a base or a salt of alkaline reaction, the ionization of the water is diminished so much that the oxygen can find almost no hydrogen ions with which to form hydroxyl ions; therefore the iron does not send any more ions (§§ 276 and 277) into the solution and rusting is greatly retarded.

Iron dissolves readily in hydrochloric and sulphuric acids with the evolution of hydrogen. At red-heat it decomposes water but the oxide is also reduced by hydrogen, so that an equilibrium results:



In nitric acid (not too concentrated) iron dissolves readily with the evolution of nitric oxide, NO, but if the iron is first dipped in concentrated nitric acid and then rinsed off it becomes indifferent to the action of nitric acid. The cause of this so-called "passivity" of iron is probably the same as for the passive modification of chromium (§ 293).

Iron forms two sets of salts, the *ferrous* and the *ferric*.

### Ferrous Compounds.

**306.** In the ferrous condition iron has only basic properties.

**Ferrous oxide**, FeO, is obtained by reducing ferric oxide with carbon monoxide. It is a black powder, which oxidizes easily on warming. **Ferrous hydroxide**, Fe(OH)<sub>2</sub>, is precipitated from ferrous salt solutions as a pale green gelatinous substance by the addition of an alkali; it oxidizes very rapidly in the air to ferric hydroxide.

**Ferrous chloride**, FeCl<sub>2</sub>, is formed on dissolving iron in hydrochloric acid; it crystallizes from this solution in green monoclinic prisms containing four molecules of water. The anhydrous salt is obtained as a white sublimate when iron is heated in dry hydrochloric acid gas. With potassium chloride and ammonium chloride ferrous chloride forms well crystallized double salts, e.g. FeCl<sub>2</sub>·2KCl + 2H<sub>2</sub>O.



**Ferrous sulphate**,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$  (*green vitriol*, *copperas*), is the most familiar ferrous salt. It is prepared commercially by partially roasting pyrite, whereby ferrous sulphide,  $\text{FeS}$ , is formed; the latter is left exposed to the air, when it oxidizes gradually to ferrous sulphate, which can be dissolved out. It crystallizes in large, bright green, monoclinic prisms, which effloresce slightly and at the same time become coated with a brown layer of basic ferric sulphate. The double salts such as  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 + 6\text{aq}$ , *MOHR'S salt*, are not so liable to oxidation; for this reason use is frequently made of Mohr's salt to standardize permanganate solutions (§ 301). Iron vitriol has numerous uses, e.g. for making ink, in dyeing, as a disinfectant (it absorbs both ammonia and sulphuretted hydrogen and is therefore used to dispel bad odors), etc., etc.

**Ferrous carbonate** is somewhat soluble in water containing carbonic acid and is therefore often present in natural waters (§ 17). The basic carbonate which is precipitated from a ferrous solution by soda oxidizes rapidly in the air to ferric hydroxide. The latter is also deposited from chalybeate waters on standing in the air for a time. Ferrous carbonate is only known as a mineral (*siderite*, § 302).

### Ferric Compounds.

**307.** The ferric ion has only very slightly basic properties. Ferric salts of weak acids such as carbonic acid do not exist. In aqueous solution most of the ferric salts, even those of strong acids, are partially hydrolyzed. They are readily converted into ferrous salts by reducing agents.

**Ferric oxide**,  $\text{Fe}_2\text{O}_3$ , iron sesquioxide, is formed on heating various iron compounds in the air and is manufactured by igniting green vitriol (§ 79). It is a dark red powder and finds use as a pigment (*colcothar*) and in polishing glass, etc.

**Ferric hydroxide** separates out as a reddish-brown hydrogel,  $\text{Fe}_2\text{O}_3 + n\text{H}_2\text{O}$ , when a ferric salt solution is treated with an alkali. The freshly precipitated hydrogel dissolves in a solution of ferric chloride or acetate. If this solution is dialyzed, a pure colloidal solution of the hydroxide is finally obtained; from this the hydrogel is reprecipitated by a small amount of alkali or acid.

**Ferrous ferric oxide**,  $\text{Fe}_3\text{O}_4$ , also called ferroso-ferric oxide or

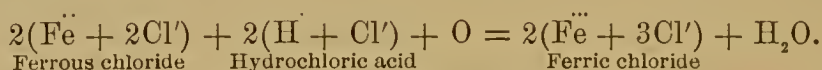
magnetic iron oxide, occurs in nature as *magnetite*. It is produced by heating iron in steam (§ 305).

**Ferric chloride** is obtained by passing chlorine into a solution of ferrous chloride. It crystallizes at different temperatures with different amounts of water. On heating the salt hydrochloric acid escapes with the water of crystallization. Anhydrous ferric chloride can be prepared by heating iron in a current of dry chlorine.

Between 320° and 440° the vapor density is approximately that calculated for  $\text{Fe}_2\text{Cl}_6$ ; between 750° and 1050° it falls to half, indicating a splitting off of chlorine.

**Ferric sulphate**, obtained by dissolving ferric oxide in sulphuric acid, forms alums, e.g. potassium iron alum,  $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ .

When a ferrous salt is converted into a ferric salt in aqueous solution the bivalent ferrous ion is transformed into a trivalent ferric ion. The oxygen required for the conversion serves to oxidize the hydrogen ions of the acid (which must be added) to water, whereupon these hydrogen ions surrender their charge to the iron ions:



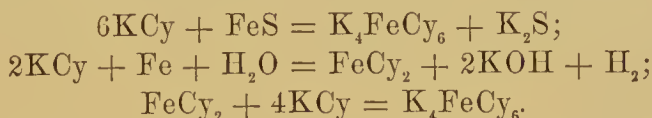
Inversely, the reduction of ferric salts to ferrous salts can be explained by supposing that every ferric ion gives up a third of its charge to another atom and thus makes the latter an ion or discharges it.

Salts of iron are also known which are derived from the hypothetical oxide  $\text{FeO}_3$ . They are obtained by heating iron filings with saltpetre or passing chlorine into an alkaline suspension of the ferric oxide hydrogele. From such solutions **potassium ferrate**,  $\text{K}_2\text{FeO}_4$ , crystallizes out in dark red prisms, isomorphous with the chromate and sulphate of potassium. These crystals are readily soluble in water but their dark red solution soon decomposes with the separation of ferric hydroxide and oxygen gas. The free ferric acid is unknown.

**308.** Iron unites with cyanogen to form complex and unusually stable anions, viz. the *ferrocyanic* ion  $(\text{FeCy}_6)'''$  and the *ferricyanic* ion  $(\text{FeCy}_6)''$ . Their best-known salts are potassium ferrocyanide,  $\text{K}_4\text{FeCy}_6 + 3\text{H}_2\text{O}$ , and potassium ferricyanide,  $\text{K}_3\text{FeCy}_6$ , the yellow and red prussiates of potash, re-

spectively. The ionization of the complex ions themselves is so slight that they give none of the ordinary reactions for iron.

For the commercial *manufacture of yellow prussiate of potash* two processes are used: In the first animal refuse (e.g. blood) is charred, yielding a black, highly nitrogenous mass. This is ignited with potash and iron filings. After cooling, hot water is added and the mixture filtered; from this filtrate the yellow prussiate crystallizes out on standing. This salt is not formed until the ignited mass is treated with water, for yellow prussiate is decomposed by heat and cannot therefore be present in the ignited mass. The latter probably contains potassium cyanide, iron and iron sulphide (animal refuse always contains sulphur compounds). These substances can interact according to the equations:



The second process is employed in illuminating-gas factories, for the unpurified gas contains a little cyanogen and prussic acid. After being freed from tar and ammonia it is passed through a washer (scrubber) containing a solution of potash in which ferrous carbonate (ferrous sulphate + potassium carbonate) is suspended. This liquid reacts with the two compounds named to form yellow prussiate and the latter can be obtained by concentration and crystallization.

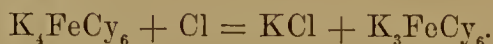
**Potassium ferrocyanide**,  $\text{K}_4\text{FeCy}_6 + 3\text{H}_2\text{O}$ , forms large sulphur-colored crystals. Its three molecules of water can be expelled by gently warming, whereupon the salt is left as a white powder. It is not poisonous. With dilute sulphuric acid it produces prussic acid on warming; with concentrated sulphuric acid it yields carbon monoxide.

The free **ferrocyanic acid**,  $\text{H}_4\text{FeCy}_6$ , separates out as a white crystalline precipitate when concentrated hydrochloric acid is added to a strong solution of potassium ferrocyanide. The precipitate soon turns blue in the air on account of the formation of Prussian blue (and partial decomposition as well). Various salts of this acid have characteristic colors and are insoluble; hence potassium ferrocyanide finds use in analysis. It is an interesting fact that this compound of iron can serve as a distinguishing

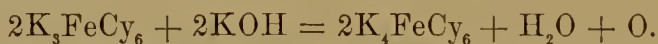
reagent for ferrous and ferric compounds. The ferrous salt of ferroeyanic acid is white but in the presence of air it passes rapidly over into the blue ferric salt (*Prussian blue*—a valuable pigment). The copper salt (§ 40) is brownish red, the zinc salt white, etc.

**Sodium nitro-prusside**,  $\text{Na}_2\text{FeCy}_5(\text{NO}) + 2\text{H}_2\text{O}$ , is formed by the action of nitric acid on sodium ferroeyanide. It crystallizes in ruby-red prisms and is a delicate reagent for alkali sulphides, whose solutions it colors violet.

**Potassium ferricyanide**,  $\text{K}_3\text{FeCy}_6$ , red prussiate, is formed from the yellow prussiate by treating a solution of the latter with chlorine or bromine:



It appears in dark-red crystals, which are readily soluble in water. The aqueous solution is unstable. It is often employed as an oxidizing-agent in alkaline solution, being itself converted into the ferroeyanide:



Iron forms some very peculiar compounds with carbon monoxide:  $\text{Fe}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ . They are produced when carbon monoxide is passed over finely-divided iron at  $80^\circ$ , or at ordinary temperatures if the gas is under pressure. Iron vessels which have held compressed illuminating-gas for some time are more or less attacked by the carbon monoxide of the gas, for if gas which has been kept in such a vessel is allowed to escape through a hot glass tube an iron mirror is formed on the inside of the tube.

## COBALT AND NICKEL.

### Cobalt.

**309.** The two best-known minerals of this metal are *smaltite*,  $\text{CoAs}_2$ , and *cobaltite*, or *cobalt glance*,  $\text{CoAsS}$ . The metal is obtained by calcining these minerals and reducing the resulting cobalto-cobaltic oxide,  $\text{Co}_3\text{O}_4$ , with carbon (or hydrogen). It has a pink color and a high lustre. Sp. g. = 8.9. It is magnetic but much less so than iron. It is indifferent to the air. Hydrochloric and sulphuric acids dissolve it very slowly but it readily forms a nitrate with nitric acid.

Besides the oxide,  $\text{Co}_3\text{O}_4$ , just referred to there are two others, **cobaltous oxide**,  $\text{CoO}$ , and **cobaltic oxide**,  $\text{Co}_2\text{O}_3$ . The salts are all cobaltous, corresponding to the bivalent ion  $\text{Co}$ .

## COBALTOUS COMPOUNDS.

The solutions of the salts are red; hence this is the color of the cobalt ion. The non-ionized cobalt salts are blue, e.g. the anhydrous  $\text{CoCl}_2$ , the silicate, etc. This difference in color enables us to tell readily whether a cobalt salt in solution is ionized or not. Thus in concentrated solutions, for instance, all those circumstances which reduce the ionization cause a change of color from red to blue, e.g. when a concentrated cobalt chloride solution is warmed or treated with hydrochloric acid. That the ionization may be diminished by warming was mentioned in connection with cupric chloride (§ 244).

**Cobaltous chloride**,  $\text{CoCl}_2 + 6\text{H}_2\text{O}$ , forms red monoclinic crystals, which turn blue on heating because of dehydration. **Cobalt sulphate**,  $\text{CoSO}_4 + 7\text{H}_2\text{O}$ , is obtained in dark-red monoclinic prisms and is isomorphous with  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ . It forms double salts with alkali sulphates, e.g.  $\text{K}_2\text{SO}_4 \cdot \text{CoSO}_4 + 6\text{H}_2\text{O}$ . **Cobalt nitrate**,  $\text{Co}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ , appears in red hygroscopic prisms. **Cobalt silicate** is very deep blue; hence its use for coloring glass. Pulverized cobalt silicate serves as a pigment (*small*) in painting, etc. THÉNARD'S *blue* is a pigment, obtained by igniting cobalt salts with alumina.

## COBALTIC COMPOUNDS.

**310. Cobaltic oxide**,  $\text{Co}_2\text{O}_3$ , is obtained by igniting cobalt nitrate. It is a black powder, which passes over into cobaltocobaltic oxide,  $\text{Co}_3\text{O}_4$ , at red heat and at white heat yields cobaltous oxide. It has the character of a peroxide; for by the addition of sulphuric acid, it is converted into a cobaltous salt with the evolution of oxygen and it yields chlorine with hydrochloric acid. In cold dilute hydrochloric acid it dissolves, however, without generating scarcely any chlorine.

Like iron, cobalt also forms complex ions, of which those with cyanogen are very stable. There are cobalt salts corresponding in composition to the yellow and the red prussiates of potash; the salt  $\text{K}_3\text{CoCy}_6$ , **potassium cobalticyanide**, crystallizes in colorless rhombic prisms. A peculiar complex ion occurs in the **potassium cobaltic nitrite**,  $6\text{KNO}_2 \cdot \text{Co}_2(\text{NO}_2)_6 + n\text{H}_2\text{O}$ , or  $\text{K}_3 \cdot \text{Co}(\text{NO}_2)_6 + n\text{H}_2\text{O}$ . It is formed on treating a solution of a cobalt salt with potassium nitrite and acetic acid. It is a yellow crystalline pre-

eipitate, which is very slightly soluble when potassium ions are present in excess in the liquid.

Cobalt also forms numerous complex ions with ammonia (§ 317).

### Nickel.

**311.** Nickel occurs in *niccolite*,  $\text{NiAs}$ , and *nickel glance*, or *gersdorffite*,  $\text{NiAsS}$ . Especially important is the nickel silicate, *garnierite*,  $\text{H}_2(\text{Ni,Mg})\text{SiO}_4 + \text{aq} (?)$ , which was discovered by GARNIER in New Caledonia, where it occurs in enormous quantities. From this ore the nickel is obtained by a blast-furnace process similar to that for iron. The discovery of garnierite marked the beginning of a new era in the nickel industry. Much nickel is refined electrolytically.

Nickel is almost as white as silver, is very tough and has a high metallic lustre. Sp. g. = 8.8–9.1. It is feebly magnetic. It dissolves sparingly in hydrochloric and sulphuric acids but freely in nitric acid. It is permanent in the air.

It is employed in *nickel-plating* metallic objects and as a constituent of several *alloys*. German silver contains about 50% copper, 25% nickel and 25% zinc. The nickel coins of Germany and the United States consist of 75% copper and 25% nickel. The use of nickel to vary the properties of iron has already been mentioned (§ 305).

The oxides of nickel,  $\text{NiO}$  and  $\text{Ni}_2\text{O}_3$ , are very similar to those of cobalt. The *nickelous oxide*,  $\text{NiO}$ , is the only one which forms salts.

**Nickel chloride**,  $\text{NiCl}_2 + 6\text{H}_2\text{O}$ , yields green monoclinic prisms. When heated it turns yellow on account of loss of water.

**Nickel sulphate**,  $\text{NiSO}_4 + 7\text{H}_2\text{O}$ , green rhombic prisms, is isomorphous with the corresponding ferrous and other salts and also forms analogous double salts.

**Nickelic oxide**,  $\text{Ni}_2\text{O}_3$ , also behaves as a peroxide; when warmed with hydrochloric acid it yields chlorine gas and nickel chloride.

**Nickel carbonyl**,  $\text{Ni}(\text{CO})_4$ , is formed when carbon monoxide is led over finely divided nickel at ordinary temperatures. The product is a colorless, highly refractive liquid, which boils at  $43^\circ$  and congeals (crystalline) at  $-25^\circ$ . Its vapor decomposes explosively at  $60^\circ$ . When heated in the air it burns with a very sooty

flame. This compound is of aid in extracting nickel from low-grade ores.

Nickel also forms a complex ion with cyanogen. On dissolving nickel cyanide in an excess of potassium cyanide the compound  $K_2NiCy_4$  is produced; it is, however, unstable, being decomposed by hydrochloric acid with the deposition of nickel cyanide,  $NiCy_2$ .

312. A very peculiar property is exhibited by the sulphides of cobalt and nickel,  $CoS$  and  $NiS$ . Hydrogen sulphide does not precipitate these sulphides from acid solutions, but, once precipitated (by ammonium sulphide), they are not dissolved by dilute acids. This is contrary to the general rule of § 146 (see also § 73), for the sulphides should either be precipitated by hydrogen sulphide from a feebly acid solution (e.g.  $CuS$ ), which is the case when the solubility product is very small, or else, when the solubility product is larger, they should dissolve in dilute acids, e.g.  $FeS$ . This anomaly is probably due to the fact that the sulphides very soon after their formation pass over into another modification (probably a polymer). Nickel sulphide is soluble in alkali sulphides immediately upon its formation but when once deposited in the solid state it is insoluble or nearly so. This is seen when a nickel solution is treated with tartaric acid and then with an excess of sodium hydroxide, no nickelous hydroxide being precipitated. If hydrogen sulphide is passed into this solution, a very dark-colored liquid results, from which nickel sulphide is deposited only very slowly. The same is true of cobalt solutions, but only when very dilute, for otherwise the cobalt sulphide soon passes over into the insoluble modification and separates out.

### PLATINUM METALS.

313. Under this head are included the metals *ruthenium*, *rhodium*, *palladium*, *osmium*, *iridium* and *platinum*. They occur only in metallic form and are associated together in mixtures or combinations. The principal deposits are in the Ural and Caucasus, but smaller quantities are also found in California, Australia and Sumatra. The most important of these metals is platinum. The platinum ores usually contain admixtures of iron, gold, etc.

This group falls into two subdivisions: the light metals, ruthenium, rhodium and palladium, and the heavy metals

osmium, iridium and platinum. The two subgroups differ considerably in atomic weight and specific gravity:

	Light.			Heavy.		
	Ru	Rh	Pd	Os	Ir	Pt
Atomic weight.....	101.7	103.0	106	191	193.0	194.8
Specific gravity.....	12.26	12.1	11.9	22.4	22.38	21.45

A complete separation of the platinum metals from each other is extremely difficult, in the first place because their properties are very similar and in the second place because their behavior is considerably modified by their mutual presence—a fact which indicates the existence of compounds with each other. Thus, for instance, platinum dissolves readily in aqua regia and pure iridium is insoluble in it; nevertheless, when an alloy of the two metals is treated with aqua regia, some of the iridium is carried into solution. Farther, the presence of iron (which occurs in all platinum ores) is often very disturbing; for example, pure platinum solutions are not precipitated by soda or barium carbonate, but if iron is present more or less platinum comes down with the hydrate of iron. In spite of these difficulties platinum, palladium, rhodium and iridium can now be purchased in a remarkably pure state.

Platinum is the easiest to obtain pure from its ores. The latter are first treated with dilute aqua regia, whereby chiefly gold is dissolved out; then with the aid of concentrated aqua regia the platinum, palladium, iridium and small amounts of the other platinum metals are dissolved; the residue is *osmium-iridium* together with some of the other metals and varying amounts of platinum. The solution contains the following compounds:  $\text{PtCl}_4$ ,  $\text{IrCl}_4$ ,  $\text{Rh}_2\text{Cl}_6$ ,  $\text{PdCl}_2$ , and very small amounts of Os and Ru, also as chlorides. If this solution is boiled with sodium hydroxide,  $\text{IrCl}_4$  is converted into  $\text{Ir}_2\text{Cl}_6$  and  $\text{NaClO}$  formed at the same time. By the addition of a few drops of alcohol the sodium hypochlorite is reduced to the chloride. Thereupon  $\text{NH}_4\text{Cl}$  is added and the platinum alone is precipitated, separating out as  $(\text{NH}_4)_2\text{PtCl}_6$ , which yields metallic platinum on heating.

### Ruthenium.

314. This steel-gray metal is hard, very brittle and very difficult to fuse, a temperature of at least  $1800^\circ$  being necessary. Even when finely divided it is but very sparingly soluble in aqua regia, forming  $\text{Ru}_2\text{Cl}_6$ , but when alloyed with platinum, it dissolves readily. The compound



$\text{RuCl}_4$  is known only in double salts. As a powder the metal oxidizes in the air to  $\text{RuO}$  and  $\text{Ru}_2\text{O}_3$ . Ruthenium also forms characteristic salts, in which it plays the part of an acid.

Potassium ruthenate,  $\text{K}_2\text{RuO}_4$ , results from fusing ruthenium with caustic potash and salpêtre. It crystallizes with  $1\text{H}_2\text{O}$  in black prisms of a greenish lustre. With water it forms a dark orange-colored solution. Its conduct reminds one of potassium manganate, for under the influence of dilute acids it is converted into potassium perruthenate,  $\text{KRuO}_4$ , with the simultaneous precipitation of a black oxide,  $\text{Ru}_2\text{O}_3$  (or  $\text{RuO}_2$ ?). It crystallizes in black octahedrons of metallic lustre, which dissolve in water to a dark green solution. A peculiar compound is the tetroxide,  $\text{RuO}_4$ , which volatilizes when chlorine is passed into the concentrated solution of potassium ruthenate. It can be solidified by cooling, when it forms a golden crystalline mass, fusible at  $25.5^\circ$ . There is no acid corresponding to this oxide.  $\text{RuO}_4$  is used for the preparation of pure ruthenium.

### Osmium.

This metal is very analogous to ruthenium; it melts as high as  $2500^\circ$ . The chlorides  $\text{OsCl}_2$  and  $\text{OsCl}_4$  and the oxides  $\text{OsO}$ ,  $\text{Os}_2\text{O}_3$  and  $\text{OsO}_2$  are known. The great similarity to ruthenium is especially noticeable in the highest oxides. Thus fusion with caustic potash and salpêtre produces potassium osmate,  $\text{K}_2\text{OsO}_4$ , which crystallizes from aqueous solution in dark violet octahedrons containing two molecules of water. The characteristic osmium compound is the tetroxide,  $\text{OsO}_4$ , formed by igniting finely powdered osmium in the air or by the action of chlorine on the metal in the presence of water. The aqueous solution of  $\text{OsO}_4$  reacts neutral but is often wrongly called osmic acid. It is employed in microscopy since organic substances (i.e. reducing-agents) precipitate black osmium. No salts derived from  $\text{OsO}_4$  are known. This compound is used in preparing pure osmium.

### Rhodium.

The metal in the fused state has the appearance of aluminium and is just as extensible (malleable and ductile) as silver. It is prepared pure in the arts by way of the chloro-purpureo rhodium chloride,  $\text{Rh}(\text{NH}_3)_5\text{Cl}_3$  (cf. § 317). Neither acids nor aqua regia affect it. When heated in the air it is oxidized to the rhodious oxide,  $\text{RhO}$ . It is able to absorb a considerable amount of hydrogen. The rhodic oxide,  $\text{Rh}_2\text{O}_3$ , yields salts with acids. Of the chlorides only  $\text{Rh}_2\text{Cl}_6$  is known; this is obtained by direct synthesis as a reddish-brown substance; it forms soluble double salts with the alkali chlorides.

### Iridium.

This very refractory metal is obtained from *iridosmine* by heating in a current of oxygen, when the osmium volatilizes as tetroxide. In the form

of a platinum alloy it is employed in the manufacture of "platinum" crucibles, dishes, distilling-vessels for the concentration of sulphuric acid (§ 86), etc. The prototype of the meter at Paris is made of an alloy of 90% platinum and 10% iridium. The admixture of iridium makes the platinum more indifferent to chemical agents. When pure, iridium is not attacked by aqua regia.

Iridium forms two chlorides,  $\text{Ir}_2\text{Cl}_6$  and  $\text{IrCl}_4$ . Both of them give double salts with the alkali chlorides; e.g.  $\text{Ir}_2\text{Cl}_6 \cdot 6\text{KCl} + 6\text{H}_2\text{O}$  and  $\text{IrCl}_4 + 2\text{KCl}$ . The former dissolves in water readily, the latter with difficulty. The tetrachloride appears as a black substance, forming with water an intensely red solution. For this reason a platinum chloride solution which contains iridium has a much deeper color than a pure solution.

### Palladium.

315. The silvery white metal fuses at  $1500^\circ$ , i.e. more easily than platinum. When finely divided it dissolves in boiling concentrated hydrochloric, sulphuric and nitric acids. On ignition in the air it is at first oxidized, thus losing its lustre, but at a higher temperature the metallic surface reappears. The most peculiar characteristic of the metal is its ability to *absorb hydrogen* in large quantities (*occlusion*). Freshly ignited palladium foil absorbs 370 times its own volume of hydrogen at room temperature. By making palladium foil the cathode in a water electrolysis apparatus the metal can be made to take up even 960 times its own volume. This absorption does not alter its metallic appearance. The absorbed hydrogen can all be expelled by heating in a vacuum.

It was formerly supposed that in this absorption a compound  $\text{Pd}_2\text{H}$  was formed. Recent investigations (by ROOZEBOOM and HOITSEMA) from the standpoint of the phase rule (§ 71) have, however, rendered the existence of this (or any similar) compound doubtful. In case a compound were formed, there would be two substances (Pd and H) and three phases (Pd, the supposed compound, and H) and we should have a complete heterogeneous equilibrium. Various states of affairs would then be possible.

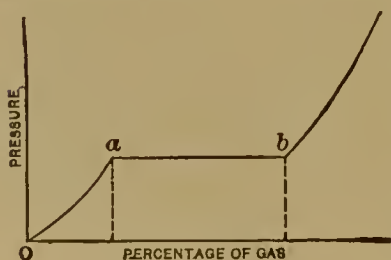


FIG. 84.

The relation between the pressure and the amount of gas at constant temperature could be represented graphically for a simple case thus: If the gas at first merely dissolves in the metal, the pressure must rise steadily with the amount of gas absorbed until the compound is formed, *a*, Fig. 84. This gas pressure must then remain constant while the absorbed gas volume increases, until the

metallic phase has completely disappeared by conversion into the hydride. Supposing that this were the case at *b*, hydrogen could still dissolve in

the hydride but the pressure of gas ought to increase from that point. At *a* and *b* the pressure curve should show abrupt bends.

On the contrary, if no compound is formed and it is merely a matter of absorption there are only two phases (gas and its solution) for the two substances and therefore the equilibrium is incomplete; the pressure must on the whole rise as the amount of gas increases and at no point will the curve suddenly change its direction.

The experiments showed that the pressure curves for various temperatures (between 0° and 190°) consist of three parts, viz., of two steep portions connected by a third middle portion, which runs almost horizontal at low temperatures. But at all investigated temperatures these portions were found to gradually pass into each other, so that the curve does not appear as in Fig. 84. These results point to the non-existence of any chemical compound; they indicate a continuous absorption, which is, however, distinguished from other known phenomena of this sort by the peculiar form of its pressure curve.

Palladium charged with hydrogen is a strong reducing-agent; chlorine and iodine are reduced by it (see § 200) to hydrogen chloride and hydrogen iodide, respectively, and ferric salts are reduced to ferrous salts.

Palladium forms two series of compounds the *-ous*, PdX<sub>2</sub>, and the *-ic*, PdX<sub>4</sub>. A characteristic compound of the first series is **palladious iodide**, PdI<sub>2</sub>, which is precipitated by potassium iodide from solutions of *-ous* salts as a black insoluble substance. This reaction is occasionally used to separate iodine from the other halogens, since their palladium compounds are readily soluble.—**Palladic chloride**, PdCl<sub>4</sub>, is produced by dissolving the metal in aqua regia. With KCl or NH<sub>4</sub>Cl it forms a difficultly soluble double chloride, K<sub>2</sub>PdCl<sub>6</sub> or (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub>. On the evaporation of its solution PdCl<sub>4</sub> dissociates into PdCl<sub>2</sub> and Cl<sub>2</sub>.

### Platinum.

**316.** This metal, which is the principal constituent of the platinum ores, is obtained pure by the process explained in § 313. It fuses at about 1770° and is extremely malleable and ductile, hence it can be made into very fine wire and very thin foil. Since it becomes soft at red heat, it can be easily worked. Alloyed with a few per cent of iridium it finds various uses. Particularly when finely divided it absorbs oxygen, a property to which is attributed the phenomenon that numerous oxidations proceed with unusual ease in the presence of platinum. When the metal is precipitated from its solutions by reducing agents, it is frequently obtained as an extremely fine velvet-black powder, *platinum black*. When the double chloride (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> is ignited the metal remains as a

porous mass—*platinum sponge*. At red heat a platinum partition allows hydrogen to pass through, while other gases are held back. This is probably due to the formation of a compound or the solubility of hydrogen in platinum. Various substances attack platinum at elevated temperatures, e.g. the hydroxides, cyanides and sulphides of the alkalis; hence these substances should not be fused in platinum vessels. This also applies to lead and other heavy metals, for they form low-melting alloys with platinum.

There are two sets of platinum compounds according to the general formula  $PtX_2$  and  $PtX_4$ . The best known platinum compound is **hydrochlorplatinic acid**,  $H_2PtCl_6$ , obtained by dissolving platinum in aqua regia. When the solution is evaporated the acid is left in the form of large reddish-brown, very hygroscopic prisms. Their aqueous solution contains the anion  $PtCl_6^{--}$ , since the platinum is deposited at the anode in an electrolysis (when ions of a metal itself exist in a solution they are always deposited at the cathode); silver nitrate does not precipitate silver chloride from the solution, which it would certainly do if free chlorine ions were present, but the compound  $Ag_2PtCl_6$ . Two characteristic salts of this acid are those of potassium and ammonium; they are very difficultly soluble in water and insoluble in alcohol; when the aqueous solution is evaporated the salt remains in the form of beautiful little octahedrons of a golden hue. The potassium salt is often made use of in determining potassium when sodium is also present, the sodium platinic chloride being very soluble, even in alcohol.

Of the remaining platinum compounds a few may be referred to. If a solution of the above acid,  $H_2PtCl_6$ , is treated with sodium hydroxide and then with acetic acid, **platinum hydroxide**,  $Pt(OH)_4$ , is precipitated. It is soluble in strong acids and also in alkalis, so that basic as well as acidic properties must be ascribed to it (*platinic acid*). Salts of this acid are moreover formed when platinum is fused with alkalis. **Platinous chloride**,  $PtCl_2$ , is produced by heating hydrochlorplatinic acid to  $200^\circ$  and in small amount also when the solution of this acid is strongly concentrated. It is a green powder, insoluble in water. With the alkali chlorides it gives soluble double salts, such as  $PtCl_2 \cdot 2NaCl$ . **Double cyanides** of platinum with many metals are also known, e.g.  $K_2PtCy_4 + 3H_2O$ ,  $BaPtCy_4 + 4H_2O$ , etc. The latter has come

into prominence because of its ability to make Röntgen rays visible. All these double salts are noted for their beautiful colors and strong dichroism.

By forming an electric arc between platinum wires under distilled water BREDIG brought about such a minute division of the platinum that the particles would pass through a filter and no distinct particles could be detected in the liquid with the aid of the most powerful microscope. A platinum liquid of this sort has a deep black color and a strong catalytic effect, which resembles in many respects the action of organic ferments. This is seen in the extremely small quantities sufficient to have a catalytic effect; for instance, 1 gram atom of platinum in 70 million liters of water accelerates the decomposition of hydrogen peroxide very perceptibly. It also follows from the fact that the catalytic effect of the platinum liquid, like that of organic ferments, alters slowly of itself but more rapidly on the addition of certain substances or on warming. Especially striking is the analogy as concerning the property of being made inactive by slight traces of certain poisons:  $10^{-6}$  gram molecule HCN in a liter is sufficient to seriously diminish the effect and corrosive sublimate acts in much the same manner.

#### AMMONIA COMPOUNDS OF THE METALS OF THE EIGHTH GROUP.

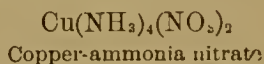
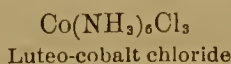
317. The elements of the eighth group, especially cobalt and platinum, besides a few elements of other groups (Cu, Cr, etc.) can form "metal-ammonia compounds." The empirical composition of these substances represents them as salts to which one or more molecules of ammonia have been added. Such compounds of cobalt are formed when ammonia is added to a solution of cobalt chloride, bromide, nitrate or the like until the precipitate first formed is redissolved. A solution of this sort absorbs oxygen from the air; if after a time some of the same acid is added from which the cobalt salt is derived, a brick-red crystalline powder separates out having the composition,  $\text{Co}_2\text{Cl}_6(\text{NH}_3)_{10} \cdot 2\text{H}_2\text{O}$ , or  $\text{Co}_2(\text{NO}_3)_6(\text{NH}_3)_{10} \cdot 2\text{H}_2\text{O}$ , for example. These compounds are termed *roseo-cobalt salts* (chloride, nitrate, etc.). They yield *purpureo-cobalt salts* when their solutions in acids are gently warmed. The latter have the composition  $\text{Co}_2\text{X}_6(\text{NH}_3)_{10}$ , where X = Cl, Br,  $\text{NO}_3$ , etc., and have a violet or purple color.—Another class of compounds is the *luteo-cobalt salts*; *luteo-cobalt chloride*,  $\text{Co}_2\text{Cl}_6(\text{NH}_3)_{12}$ , e.g., is obtained by adding ammonium chloride and an oxidizing agent (bromine) to a cobalt chloride solution rendered alkaline with ammonia. This compound crystallizes in reddish-yellow prisms, which dissolve slowly in cold water.—Farther, compounds are known which are derived from the preceding in such a way that  $\text{NO}_2$  groups replace chlorine, etc., e.g.,  $\text{Co}_2\text{Cl}_2(\text{NO}_2)_4(\text{NH}_3)_6$ , *croceo-cobalt chloride*;  $\text{Co}_2\text{Cl}_4(\text{NO}_2)_2(\text{NH}_3)_{10}$ , *xantho-cobalt chloride*;  $\text{Co}_2\text{Cl}_2$

$(\text{NO}_2)_4(\text{NH}_3)_{10}$ , flavo-cobalt chloride. They are obtained by the action of nitrous acid on ammoniacal cobalt solutions.

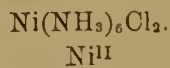
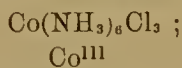
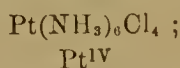
Platinum also has numerous groups of metal-ammonia compounds. Let us consider a few: If a solution of platinous chloride in hydrochloric acid is treated with ammonia, a green precipitate is formed; on boiling the mixture there is formed an insoluble compound,  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 + \text{H}_2\text{O}$ , platino-diammonium chloride (green salt of MAGNUS) and in the solution another is formed, platino-semi-diammonium chloride,  $\text{PtCl}_2(\text{NH}_3)_2$ ; both of them form salts in which bromine, iodine or  $\text{NO}_2$  appears in place of the chlorine. On heating the platino-diammonium chloride to  $220^\circ\text{--}270^\circ$  platinoammonium chloride,  $\text{PtCl}_2(\text{NH}_3)_2$ , is formed; it is yellow, crystalline and sparingly soluble in water. It can be oxidized (with chlorine) to a platinumammonium chloride,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$ ; in a similar manner platino-diammonium chloride yields a platinum-diammonium chloride,  $\text{Pt}(\text{NH}_2)_4\text{Cl}_4$ , and so on. A large number of these metal-ammonia compounds have been discovered by JÖRGENSEN.

In 1893 WERNER suggested a plan for classifying these compounds and inasmuch as his views are of general importance in inorganic chemistry a few pages at the end of this book may be devoted to the subject.

He divides the compounds in question into two classes. The first class comprises those compounds which contain six  $\text{NH}_3$  molecules for one metallic atom or are derivatives of such according to certain rules. The compounds of the second class contain four  $\text{NH}_3$  molecules to one metallic atom. As examples we may take:

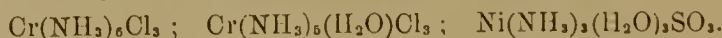


According to the valence of the metallic atom these classes can be divided into different groups; for instance, the first can be divided into:

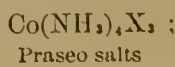
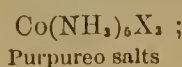
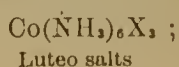


From the compounds which contain the  $\text{M}(\text{NH}_3)_6$  complex ( $\text{M}$  = metallic atom) analogous compounds can be derived by substituting  $\text{NH}_3$  molecules with others. However, *the total number of molecules in combination with the metallic salt remains six*. Particularly  $\text{H}_2\text{O}$  is capable of replacing  $\text{NH}_3$ .

The following are examples of this sort of substitution:



From the compounds just mentioned, i.e. those containing an  $\text{MA}_6$  complex (where  $\text{A}$  can be ammonia or water or another molecule), others are derived by the loss of  $\Delta$  molecules, e.g.:



The same applies to the compounds of the second class.  $\text{NH}_3$  can be substituted by various other molecules and the compounds  $\text{M}(\text{NH}_3)_4\text{X}_2$  can lose  $\text{NH}_3$  and go over into compounds which bear a definite relation to the former, e.g.:



Plato-diammine chloride



Plato-mono-diammine chloride



Platosammine chloride

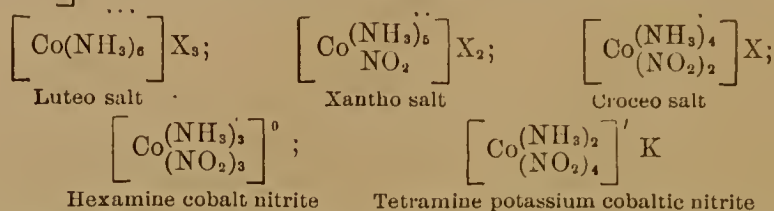
These two large classes of metal-ammonia compounds comprise all known compounds of this sort. Their classification is thus simple.

318. The loss of ammonia just referred to is accompanied by an important change in the structure of these complex compounds. Let us take the luteo-chlorides as an example in order to discuss this. Their aqueous solutions are strongly ionized, as the high electrical conductivity shows. The existing ions must be  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $3\text{Cl}^-$ , for in the first place all the chlorine can be precipitated directly with a silver solution, wherefore all three chlorine atoms must exist as ions, and in the second place the solution gives neither the ordinary reactions of cobalt nor those of ammonia. If, however, a luteo salt is converted into a purpureo salt by the loss of  $1\text{NH}_3$ , one of the halogen atoms loses at the same time the ability to act as an ion, which is evident from the fact that silver nitrate directly precipitates but two thirds of the chlorine atoms from a dissolved purpureo-chloride solution; moreover the electrical conductivity is considerably lessened. The same statements apply to the transformation of purpureo-chloride into praseo-chloride, the latter of which can be shown in a similar manner to contain only chlorine ion in aqueous solution. Finally in the hexamine salts all ionization has disappeared; the solution of hexamine-cobalt nitrite,  $\text{Co}(\text{NH}_3)_6(\text{NO}_2)_2$ , for example, was found to be practically a non-conductor.

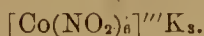
It must therefore be assumed that the solution of a luteo salt contains the trivalent ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  besides three anions; a solution of a purpureo salt, the bivalent ion  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  and two anions; a solution of the praseo salts, the univalent ion  $[\text{Co}(\text{NH}_3)_4\text{X}_2]^{+}$  and one anion; while in the hexamine compounds the complex  $[\text{Co}(\text{NH}_3)_6]^{0}$  is non-ionizable, or in other words neutral (nullivalent). Entirely analogous to this is the behavior of the compounds of the second class in their progressive loss of ammonia molecules. It is interesting in this connection to note that in the first class the number of groups, or elements substituting them, present in the complex ion in addition to the metal is always six, in the second class always four. WERNER assumes that these are directly united with the metal, while the ionizable halogen atoms or negative groups are indirectly connected with the metallic atom through ammonia.

319. Not less worthy of note is the effect of still further substitution

of ammonia by negative groups or elements. The neutral complex  $\left[ \text{Co} \begin{matrix} (\text{NH}_3)_3 \\ \text{X}_3 \end{matrix} \right]$  is then converted into a negative ion. Thus we have the series.



As the last one of the series we must regard the potassium cobaltic nitrite described in § 310 :



The number of compounds containing such a complex  $\text{MX}_6$  as trivalent ion is very large. It is here sufficient to note that potassium ferrieyanide  $\text{K}_3[\text{FeCy}_6]$  and the analogous cyanides of cobalt, iridium, rhodium, etc., belong in this category.

In the other classes where the metal is quadrivalent (Pt) or bivalent (Ni) the relations correspond throughout. Whenever a molecule of  $\text{NH}_3$  goes out, one of the negative atoms or groups enters the complex cation, which thus gradually becomes less positive and finally acts as an anion. There are also numerous compounds of this class whose composition formerly appeared to be absolutely irregular. From  $[\text{Pt}(\text{NH}_3)_6]\text{X}_4$  we obtain the indifferent platinamines  $\left[ \text{Pt} \begin{matrix} (\text{NH}_3)_2 \\ \text{X}_4 \end{matrix} \right]$ , while a substitution of the last two  $\text{NH}_3$  groups by halogen leads to the bivalent anion  $(\text{PtX}_6)''$ , which must be assumed in potassium platinum chloride and elsewhere (§ 316). In connection with these we also have analogous compounds of tin, as  $(\text{NH}_4)_2(\text{SnCl}_6)$ , pink salt, and further hydrofluosilicic acid  $\text{H}_2(\text{SiF}_6)$  and its salts, etc., etc.

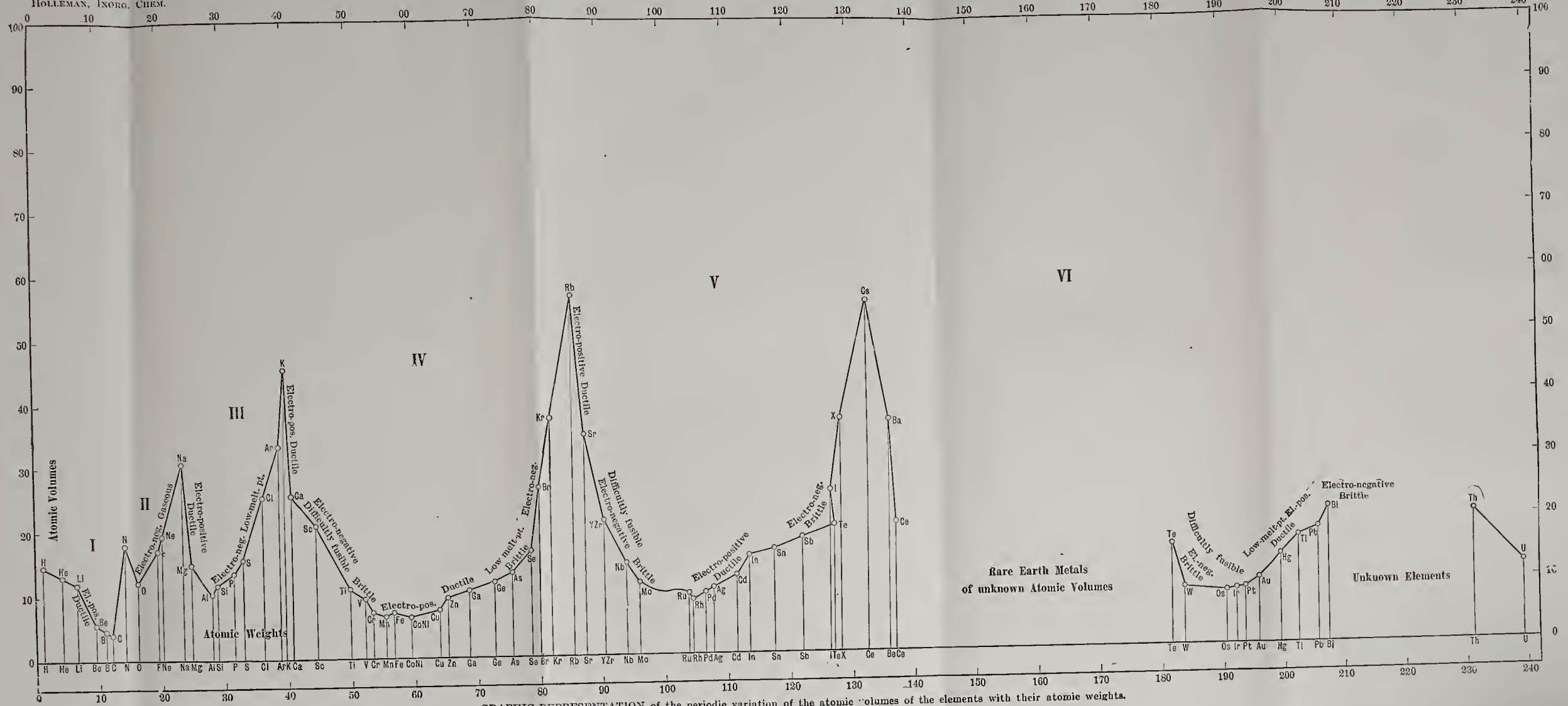
By an analogous substitution of ammonia in  $[\text{M}(\text{NH}_3)_6]\text{X}_2$  we arrive again in the third subdivision (see above) at a number of known compounds. Complete substitution of  $\text{NH}_3$  by negative groups or atoms must lead here to a quadrivalent anion and experiments show this to be true; an illustration is found in potassium ferrocyanide and its analogues.

Numerous metal-ammonia compounds and "double salts" thus come to arrange themselves in a simple classification, based on the hypothesis that *the metals in question have the property of forming complex ions with six molecules* ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , etc.) *or atoms*.

This hypothesis leads to various other conclusions, the discussion of which, however, will not be undertaken here.



HOLLEMAN, INORG. CHEM.



GRAPHIC REPRESENTATION of the periodic variation of the atomic volumes of the elements with their atomic weights.



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